California State Polytechnic University, Pomona

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Chem 315
Midterm Exam **Name: _____**
Fall, 2013
Beauchamp

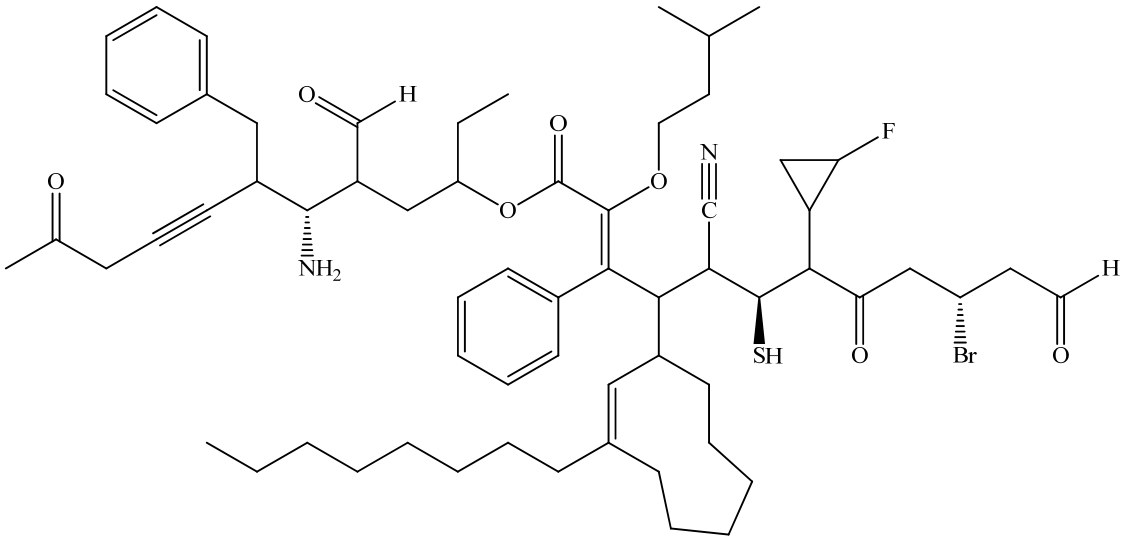
Topic	**Total Points**	**Credit**
1. Nomenclature (1)	30	
2. Tautomeric mechanisms, arrow pushing, proton transfers, resonance, one in acid and one in base	30	
3. Nucleophile and electrophile reactions OR Relative Reactivity of C=O Groups	20	
4. Reactions Page (10 three step synthetic sequences)	30	
5. Multistep syntheses using the reactions learned thus far in the course (requires multiple steps)	30	
6. Complete details of S_N1/E1 and S_N2/E2 reactions. Stereochemistry, arrow pushing, carbocations, rearrangements might be part of the problem	30	
7. Complete arrow pushing mechanisms, (1 in acid & 1 in base)	30	
Total	200	

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. Only write answers on the space available. Do your best to show me what you know in the time available.

Develop a passion for learning. If you do, you will never cease to grow.
Anthony J. D'Angelo

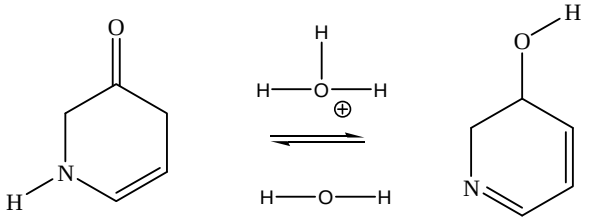
California State Polytechnic University, Pomona

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

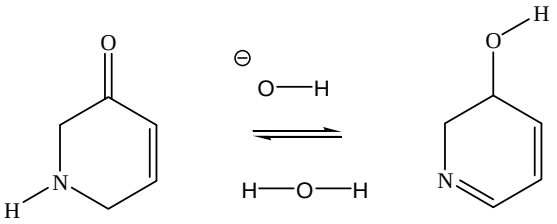


2. Provide a complete arrow-pushing mechanism (curved arrows, lone pairs and formal charge) to explain the following tautomeric transformations. (30 pts)

a.

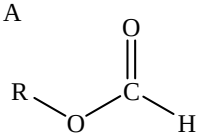


b.

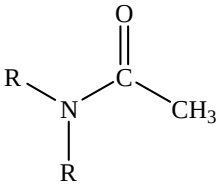


3. Order the following carbonyl compounds from strongest (= 1) to weakest and provide and explanation for your order. Show the expected products (not the mechanisms) with 1. $LiAlD_4$ 2. workup (20 pts)

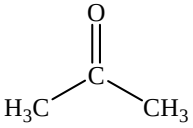
A



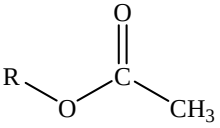
B



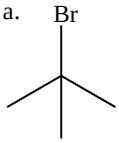
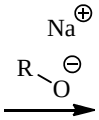
C



D



4. 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.   HBr, hν, ROOR → 1. Mg 2. CO_2 3. wk

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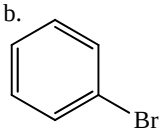
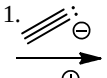
b.  1. Li 2. $H_2C{=}O$ 3. wk → CrO_3, pyridine → 1.  2. workup

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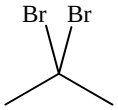
c.  1. excess $NaNR_2$ 2.  3. wk → PBr_3 → 1. NaCN 2. mild acid

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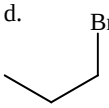
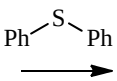
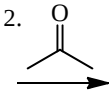
d.   → 1. n-BuLi 2.  → 1. CH_3MgBr 2. wk

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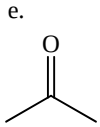
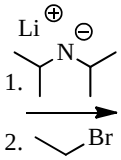
e.   → CH_3Li, 2. wk → H_2SO_4, Δ

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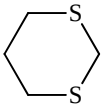
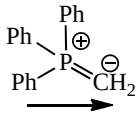
f.  1. n-BuLi 2.  → $HgBr_2$, H_2O → 

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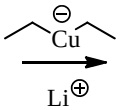
g.  1. $NaBH_4$ 2. CrO_3/H_2O → $SOCl_2$ → 

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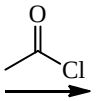
h.  $Br_2/h\nu$ → 1. NaN_3 2. $LiAlH_4$ 3. wk → 

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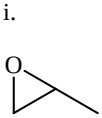
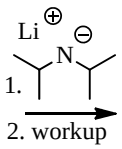
i.   → CrO_3, H_2O → 1. NaOH 2. 

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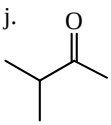
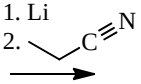
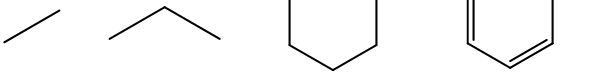
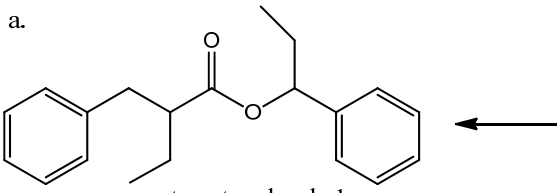
j.  1. $LiAlH_4$ 2. wk → 1. TsCl/pyridine 2. NaBr → 1. Li 2.  3. workup

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. (30 pts)

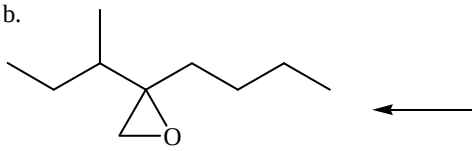
Given sources of carbon: CH_4  CO_2 NaCN

a.



target molecule 1

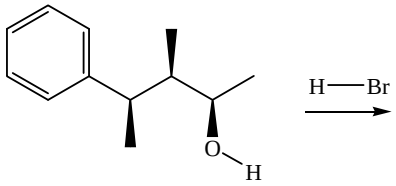
b.



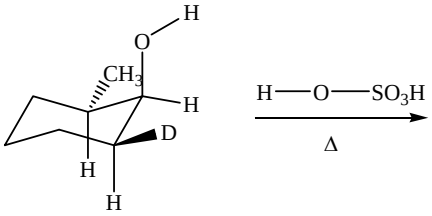
target molecule 2

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 c and d. (30 pts)

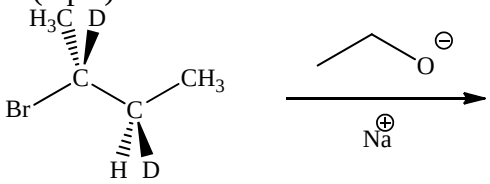
a. (10 pts)



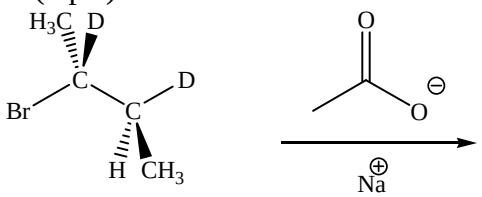
b. (10 pts)



c. (5 pts)

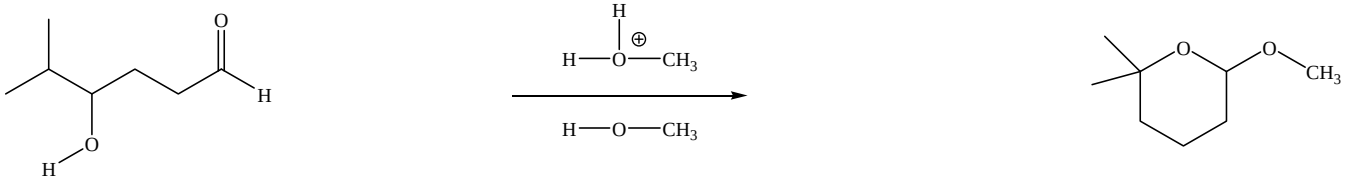


d. (5 pts)

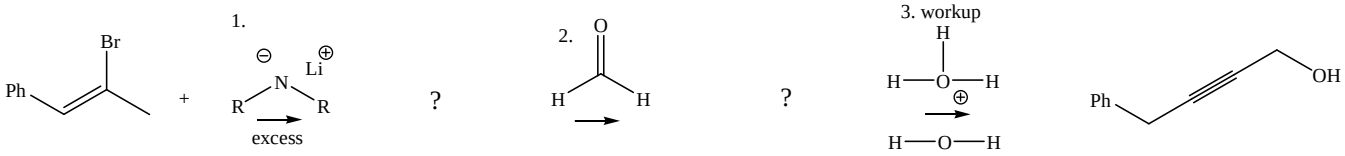


7. Provide complete arrow-pushing mechanisms for the reactions below. Include curved arrows, lone pairs of electrons and formal charge for each step. If resonance is present, draw the best resonance structure and at least one additional resonance structure to show you recognize this feature. (30 pts)

a. (Hint: Number and count the carbon atoms in the starting structure and the product. Possible in 6 steps.)



b. (Hint: Draw in hydrogen atoms. Number and count the carbon atoms. Possible in 6 steps)



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Develop a passion for learning. If you do, you will never cease to grow.
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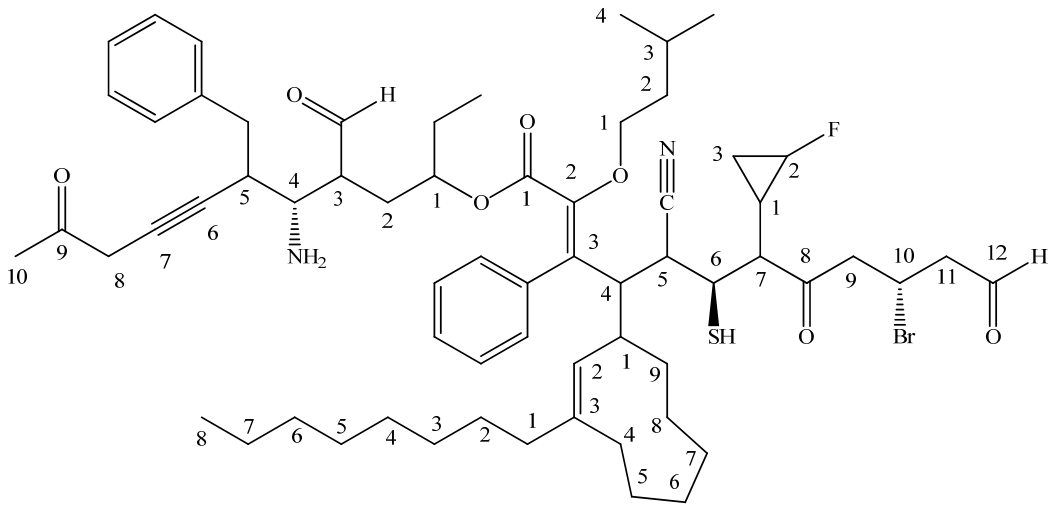
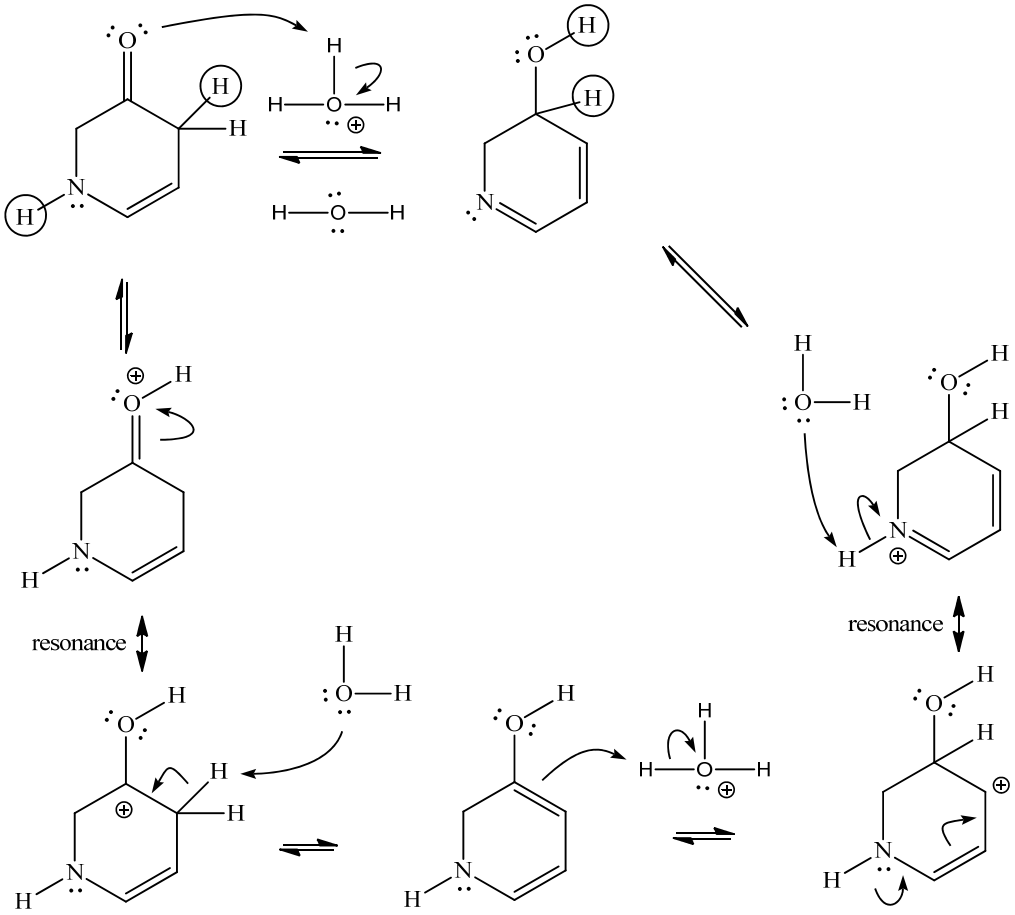
5. Provide an acceptable name for the following structures. (30 pts)



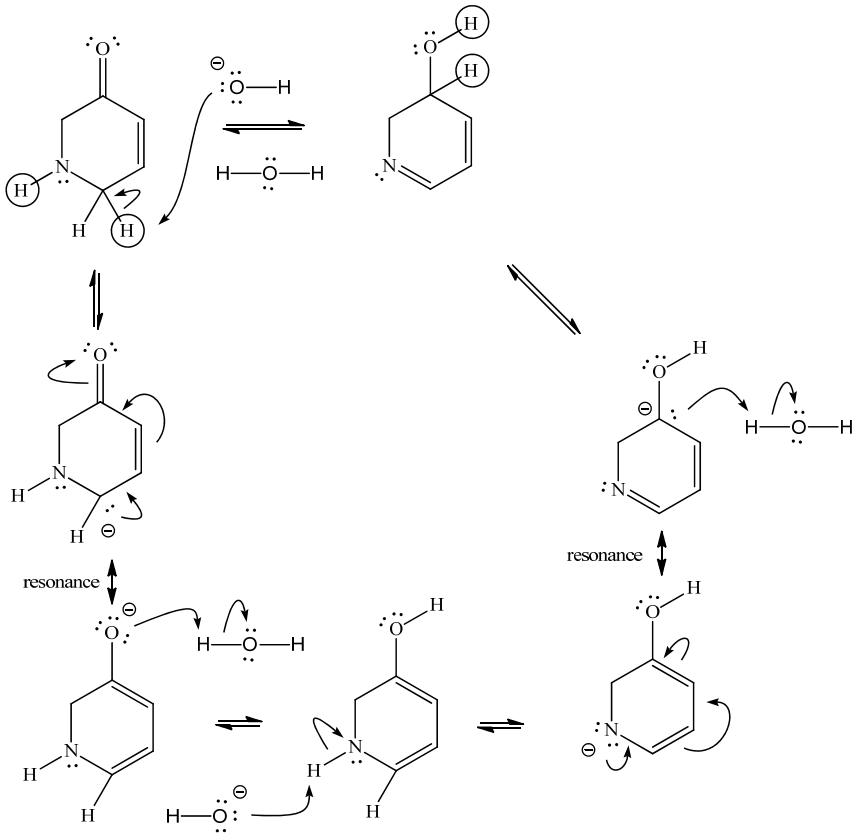
1-ethyl-3-formyl-4R-amino-5-benzyl-9-oxodec-6-ynyl 2-(3-methylbutoxy)-3-phenyl-4-(3-octylcyclonon-2Z-enyl)-5-cyano-6S-mercapto-7-(2-fluorocyclopropyl)-8,12-dioxo-10S-bromododec-2E-enoate

6. Provide a complete arrow-pushing mechanism (curved arrows, lone pairs and formal charge) to explain the following tautomeric transformations. (30 pts)

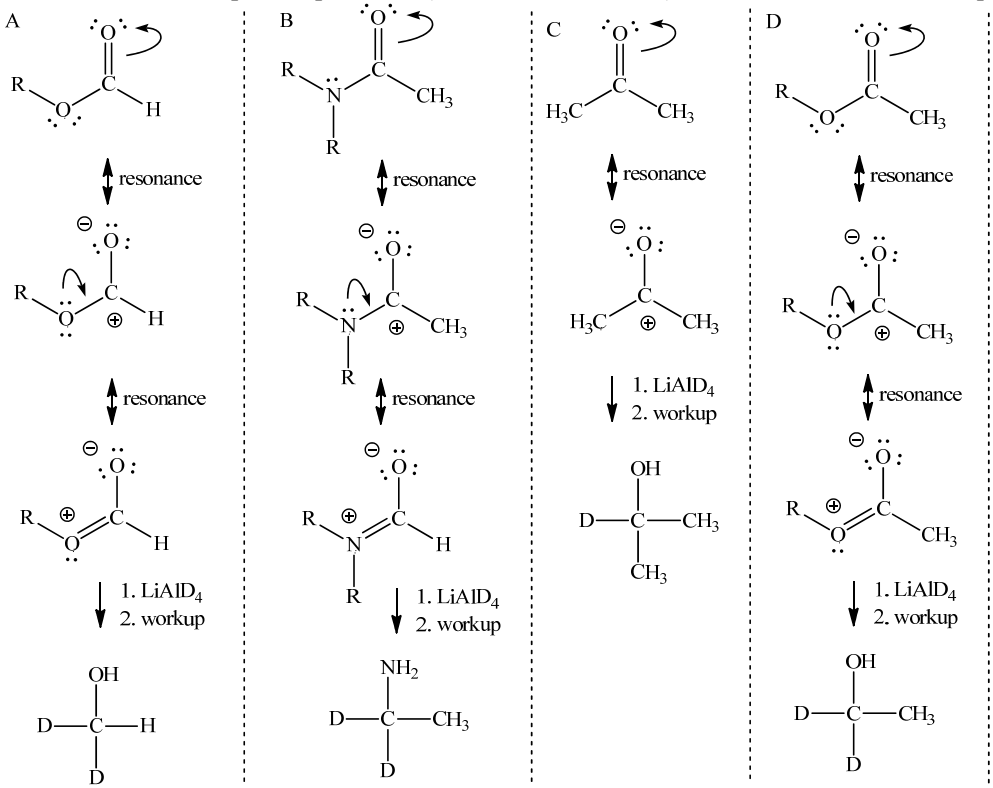
a.



b.



7. Order the following carbonyl compounds from strongest (= 1) to weakest and provide and explanation for your order. Show the expected products (not the mechanisms) with 1. $LiAlD_4$ 2. workup (20 pts)



Compounds A, B and D have an extra resonance structure that moves the positive charge off of the carbon atom. Since this charge attracts the negative nucleophile we expect these to be less reactive. So compound C (ketone) is the most reactive electrophile. Since B has a nitrogen atom donating its electrons, it should be much better than A or D in sharing to form the third resonance structure and the amide should be least reactive. The difference between A and C is H versus R at the electrophilic carbon atom. R is more inductively donating than H and should reduce the partial positive (less reactive) and R is larger than H which should sterically inhibit formation of the product (also less reactive). Therefore A should be more reactive than D for those reasons. The overall order of reactivity should be:

C > A > D > B

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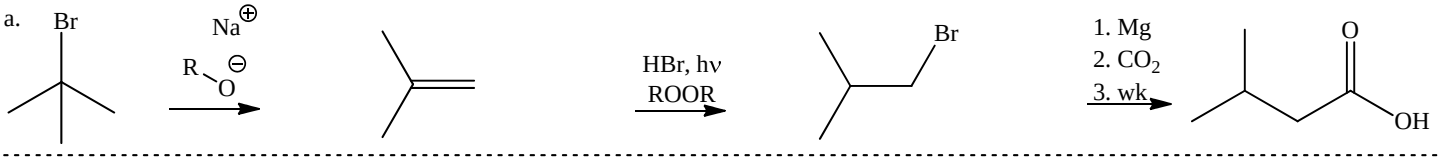
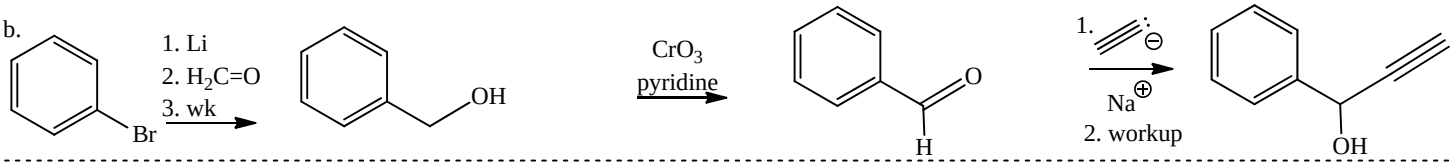
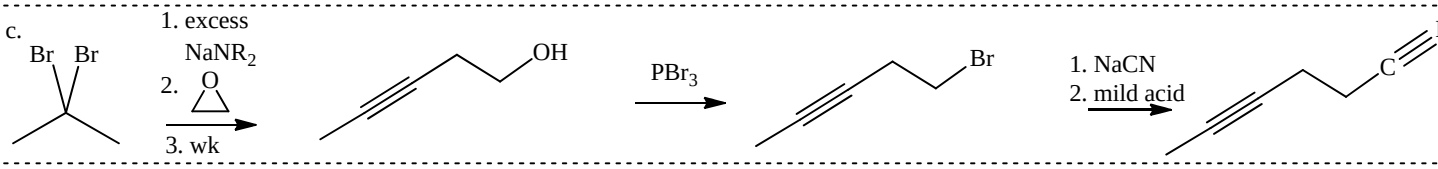
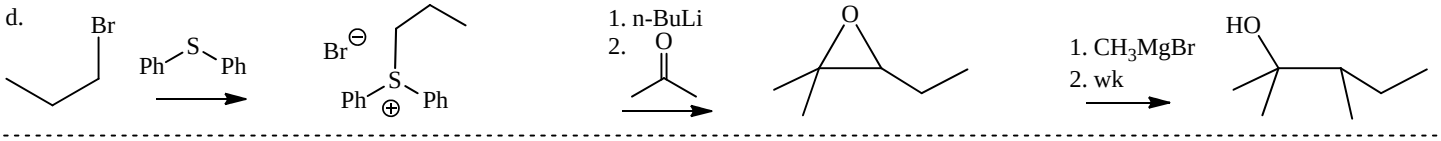
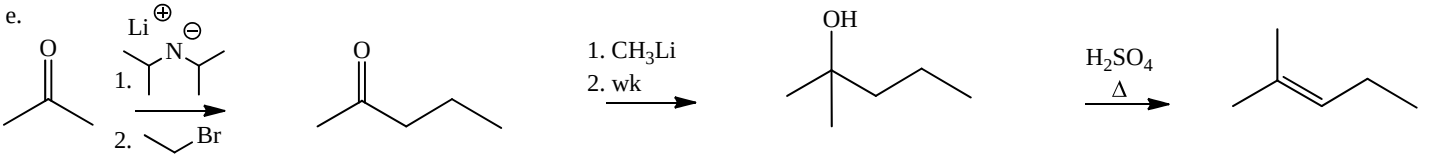
Fill in the missing product or reagent, as needed, for each reaction below. Do not waste time by writing mechanisms or thinking too much on any one part. (30 pts)

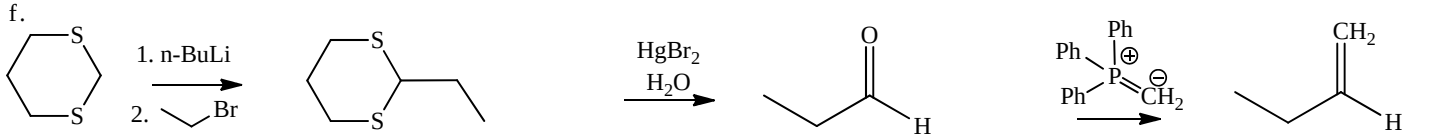
a. 

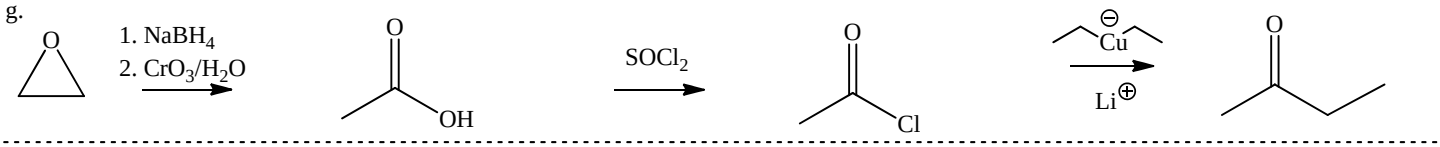
b. 

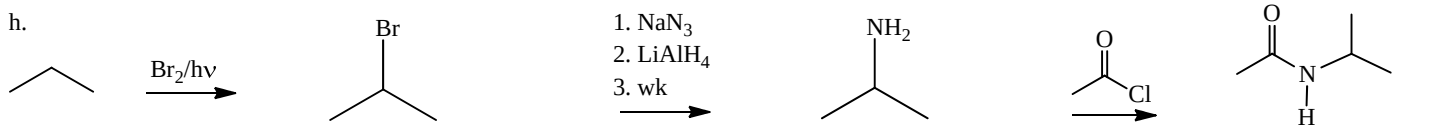
c. 

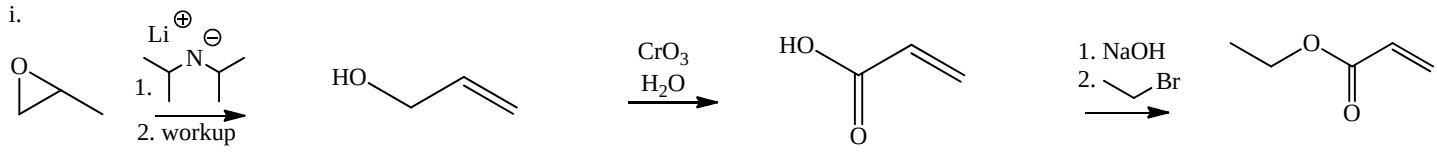
d. 

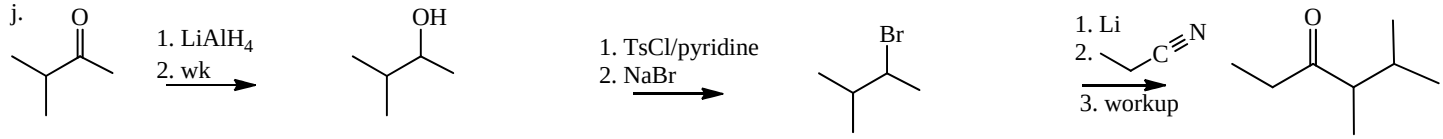
e. 

f. 

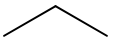
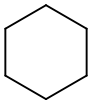
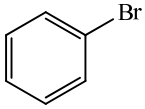
g. 

h. 

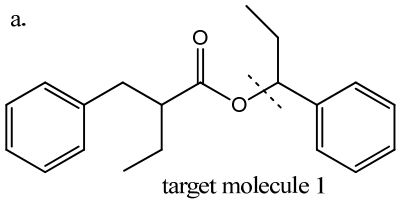
i. 

j. 

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. (30 pts)

Given sources of carbon: CH_4     CO_2 NaCN

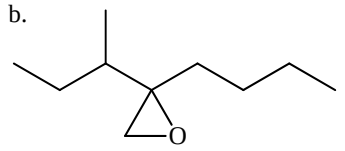
a.



target molecule 1

There are many possible approaches for both target molecules.

b.

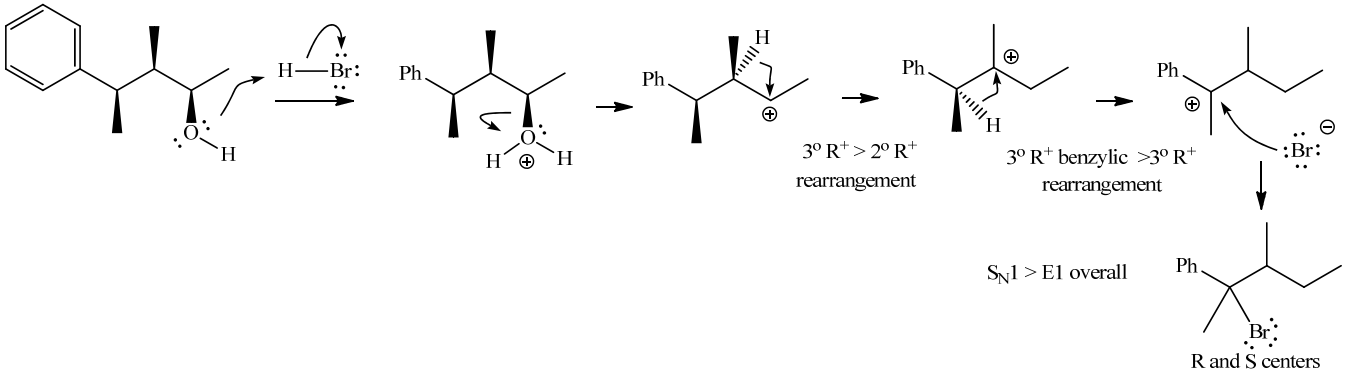


target molecule 2

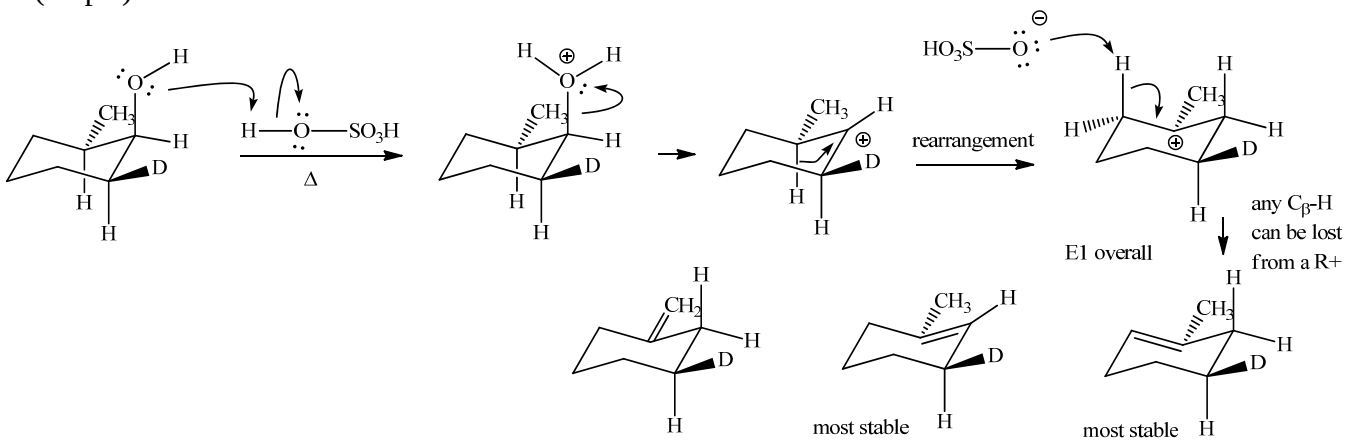
California State Polytechnic University, Pomona

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 c and d. (30 pts)

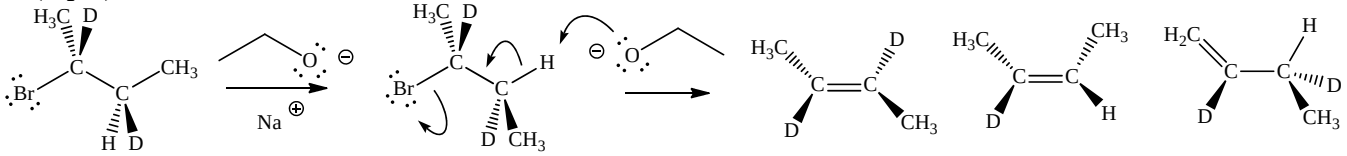
a. (10 pts)



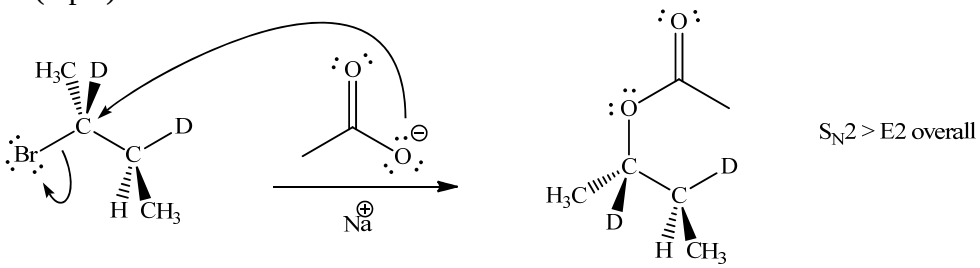
b. (10 pts)



c. (5 pts)

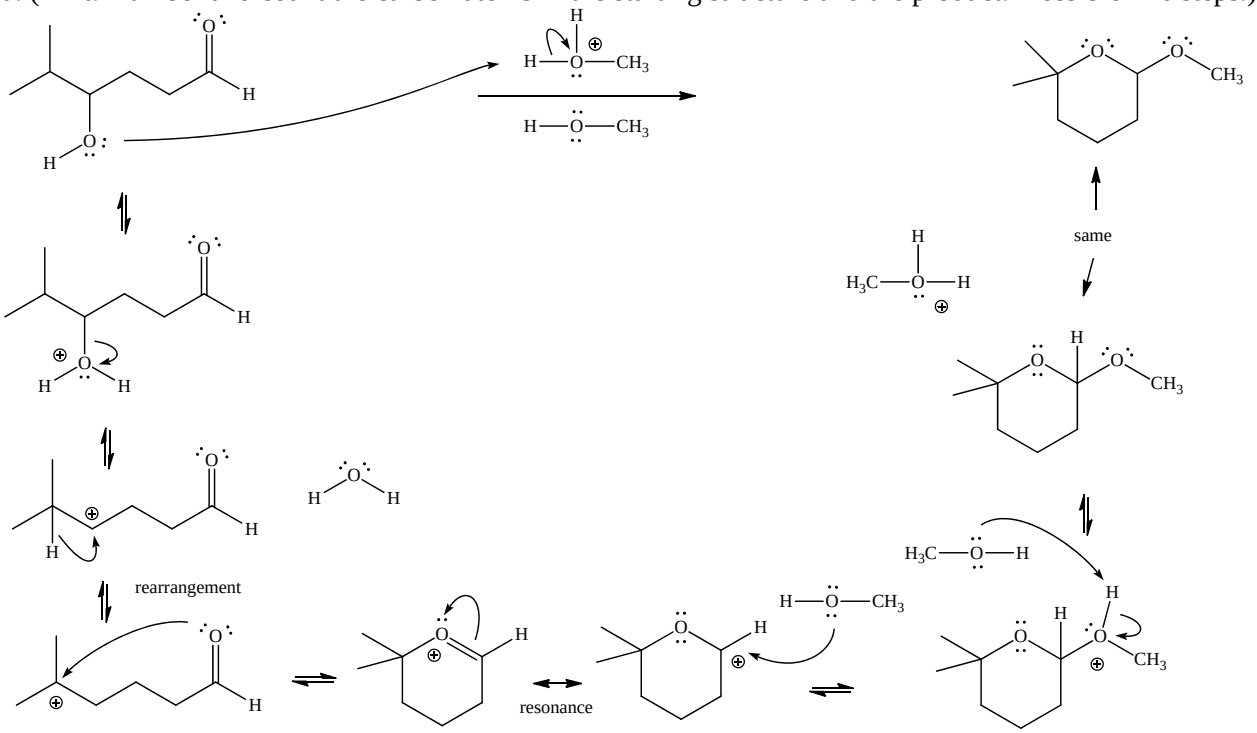


d. (5 pts)

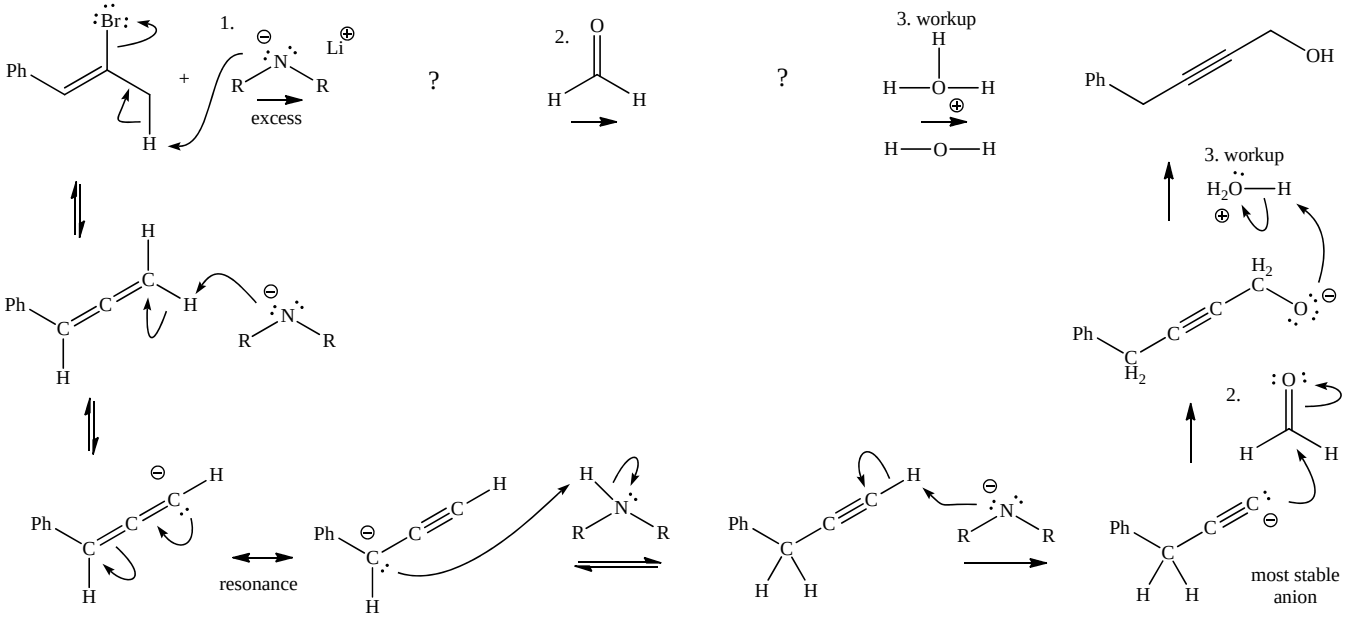


8. Provide complete arrow-pushing mechanisms for the reactions below. Include curved arrows, lone pairs of electrons and formal charge for each step. If resonance is present, draw the best resonance structure and at least one additional resonance structure to show you recognize this feature. (30 pts)

a. (Hint: Number and count the carbon atoms in the starting structure and the product. Possible in 6 steps.)



b. (Hint: Draw in hydrogen atoms. Number and count the carbon atoms. Possible in 6 steps)



Always do your best. What you plant now, you will harvest later. Og Mandino