California State Polytechnic University, Pomona

Chem 316
Final Exam
Winter, 2008
Beauchamp

Name: _____

Topic	Total Points Exam Points	Credit
1. Nomenclature (1)	30	
2. Explanation of Relative Reactivities of Aromatic Compounds or Carbonyl Compounds	20	
3. Reactions Page (10 x 3 = 30)	30	
4. Tautomers (acidic conditions and base conditions)	30	
5. Aromatic Mechanism and Explanation of Substituent Effects	30	
6. C-14 Synthesis	25	
7. Bio-organic Game (reaction recognition/simplistic mechanisms)	52	
8. Carbonyl Chemistry – synthesis and mechanisms	30	
Total	245	

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 front of each page. Do your best to show me what you know in the time available.

Nothing in life is to be feared. It is only to be understood. Marie Curie

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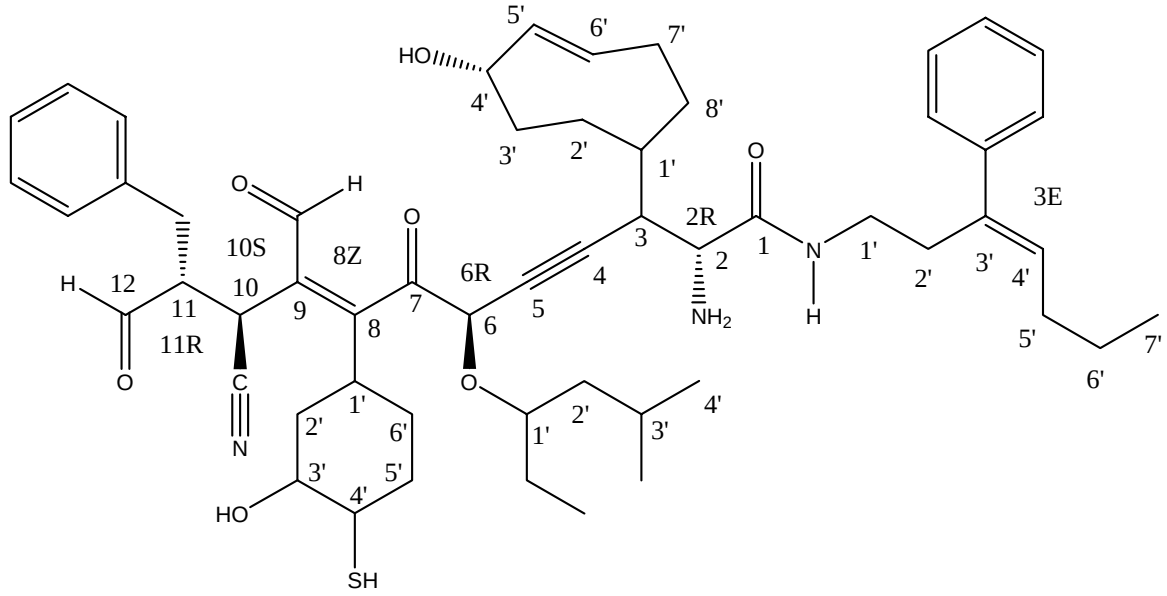
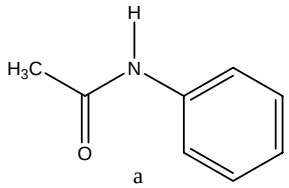
1. Provide an acceptable name for the following structure. (30 pts)

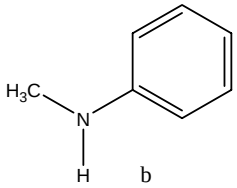


(2R,6R,10S,11R)-*N*-(3-phenylhept-3E-enyl)-2-amino-3-(4-hydroxycyclooct-5E-enyl)-6-(1-ethyl-3-methylbutoxy)-7,12-dioxo-8-(3-hydroxy-4-mercaptocyclohexyl)-9-formyl-10-cyano-11-benzyldodec-8Z-en-4-ynamide

2. State whether each of the following aromatic substituents acts as an activating or deactivating group on the aromatic ring. Order the substituents in decreasing order of activating influence on the aromatic ring (1 = most activating). Show intermediate structures that will explain your order of reactivity. Write out the reaction conditions for bromination and an expected major product in each case. (20 pts)



a



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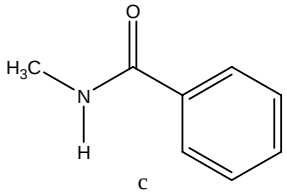

c

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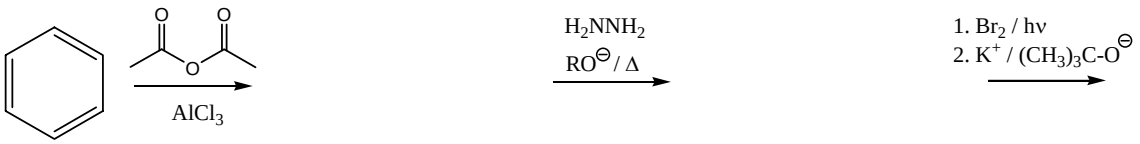
3. Provide the expected product for each of the following transformations. Show regiochemistry and stereochemistry clearly, if relevant. Do NOT show mechanisms. WK = workup. (30 pts)

a.



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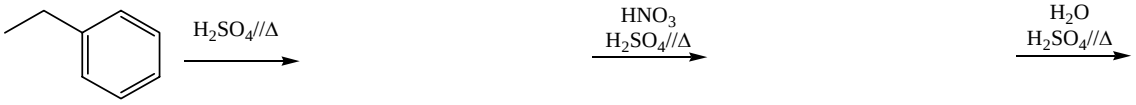

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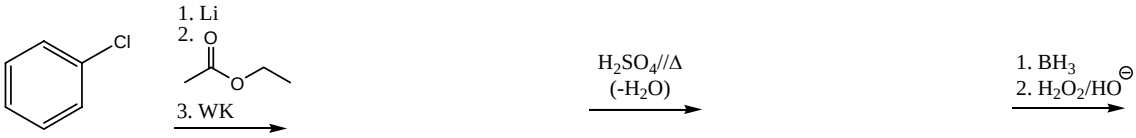

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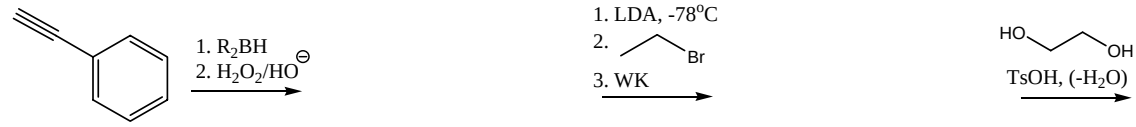

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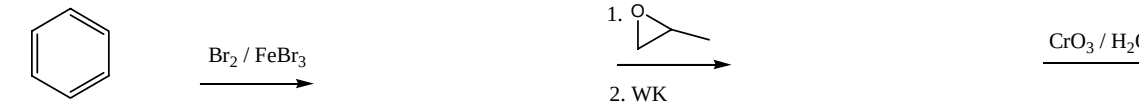

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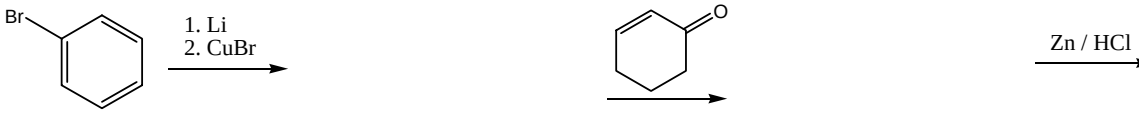

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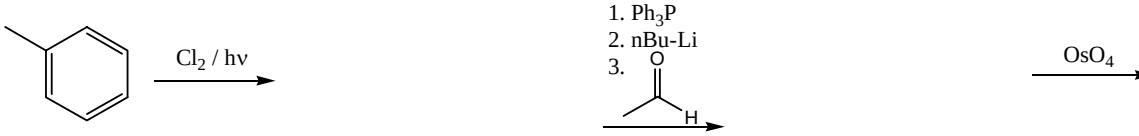
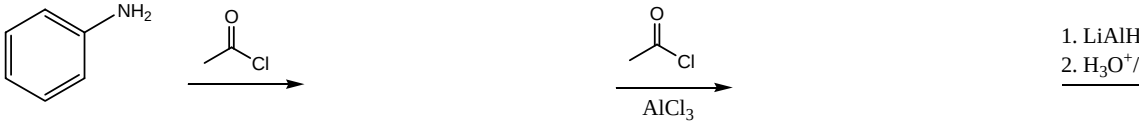


i.



j.

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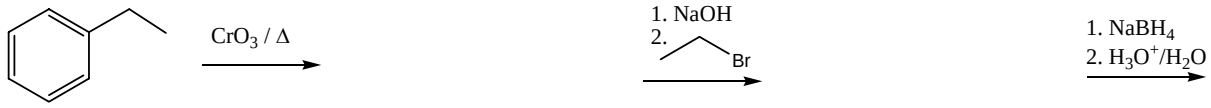


4. Starting from benzene, propose a synthesis for each of the following molecules. (25 pts)

a. Synthetic targets – Propose a synthetic sequence that leads to each molecule. No mechanisms are required here. (4 pts)

i.

ii.

b. Provide mechanisms that show how any necessary electrophiles reacting with the aromatic ring are generated. (6 pts)

i.

ii.

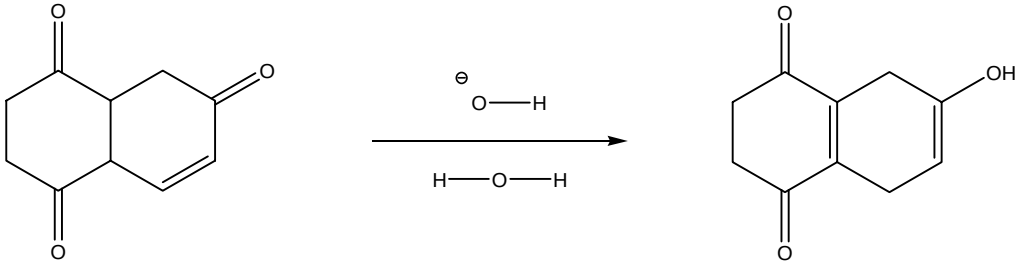
c. Provide a mechanistic explanation that explains the observed regioselectivity (ortho, meta or para) when the second group adds to the aromatic ring in each of your proposed syntheses in part a. (20 pts)

i.

ii.

5. Provide a complete arrow-pushing mechanism for each reaction below. Include curved arrows, lone pairs of electrons and formal charge. If resonance is present, draw at least one additional resonance structure to show you recognize this feature, and one of them should be the "best" resonance structure. (35 pts – base = 15 pts and acid = 20 pts)

a.



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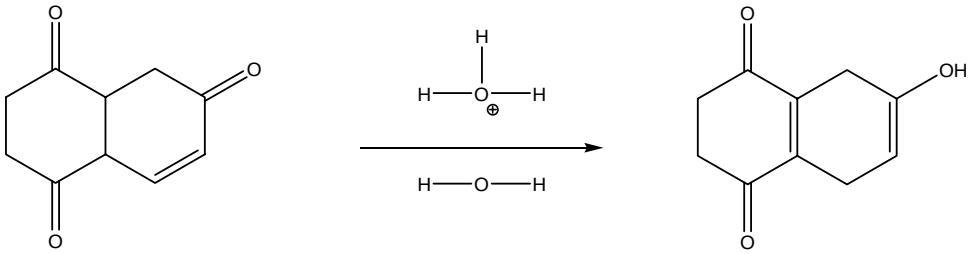
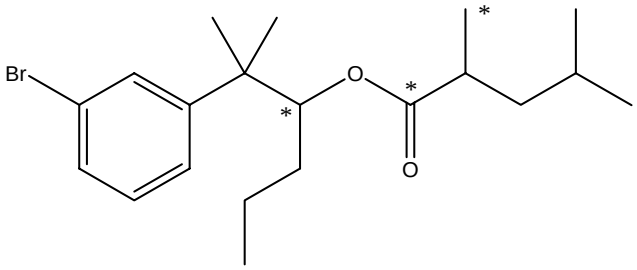


6. Propose a synthesis for the following compound using methane, ethane, propane, cyclohexane, benzene, sodium cyanide and/or carbon dioxide. Your only sources of radioactive ^{14}C carbon are methane, $*CH_4$, carbon dioxide, $*CO_2$ and sodium cyanide, Na*CN. You may also use any typical organic reagents. Often the best strategy is to work backwards from the target molecule. The last step of the synthesis should be your first step. Show the reagents and reactant for each backwards step until you reach allowable starting molecules. Do not show mechanisms. (30 pts)

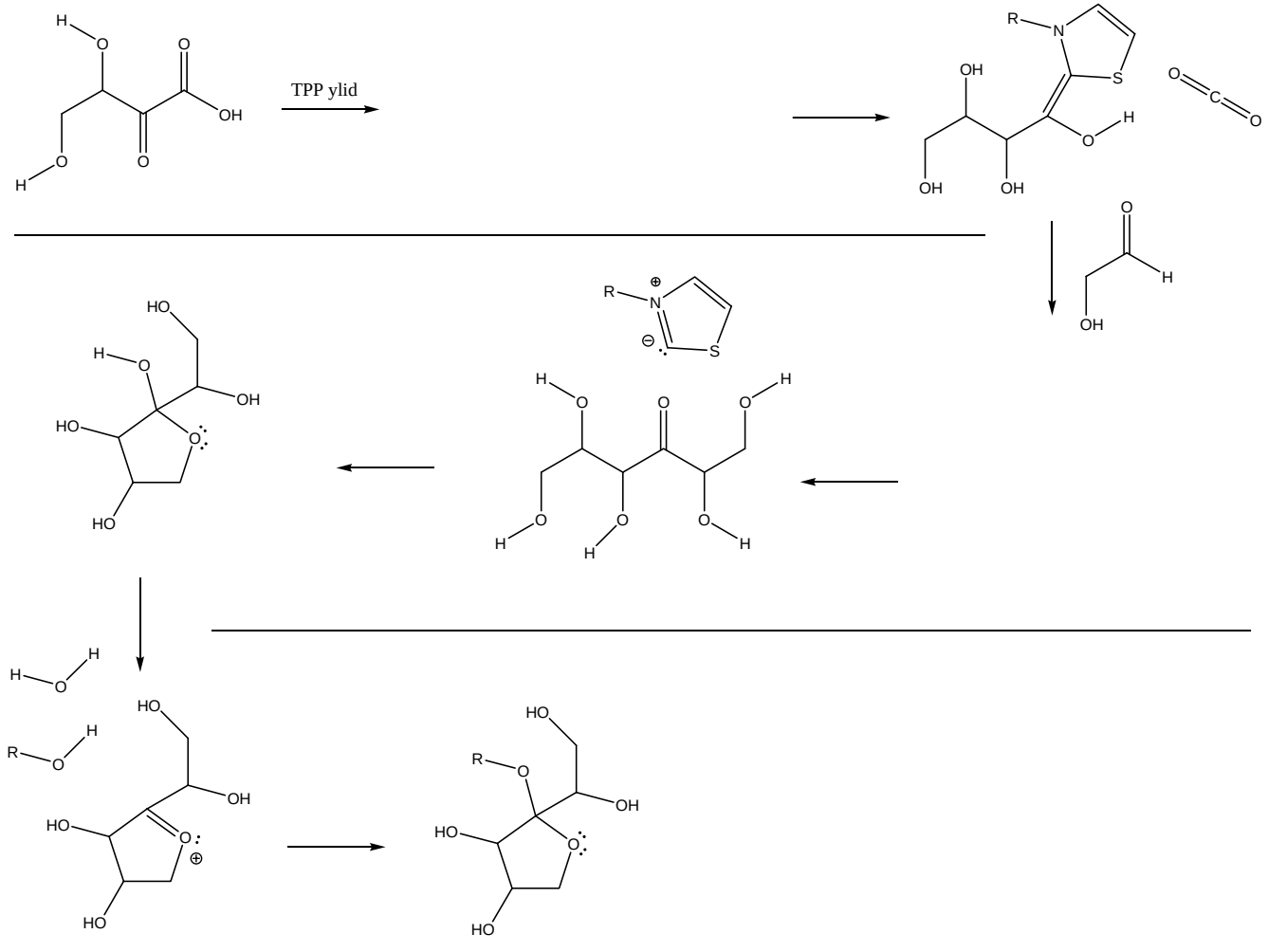


7. From the given bio-organic structure, use our simplistic mechanisms to show how each transformation could occur. If any structures are missing, use the descriptive term to fill in the necessary structures and details. Draw in any additional atoms or structures needed to demonstrate the transformations (e.g. a hydrogen atom or a water molecule, any co-factors, etc.). Use **B:** if you need a base and **B-H⊕** if you need an acid. **Acceptable representations of possible co-factors are provided at the bottom of the last page.** (50 pts)

a.

b

c.



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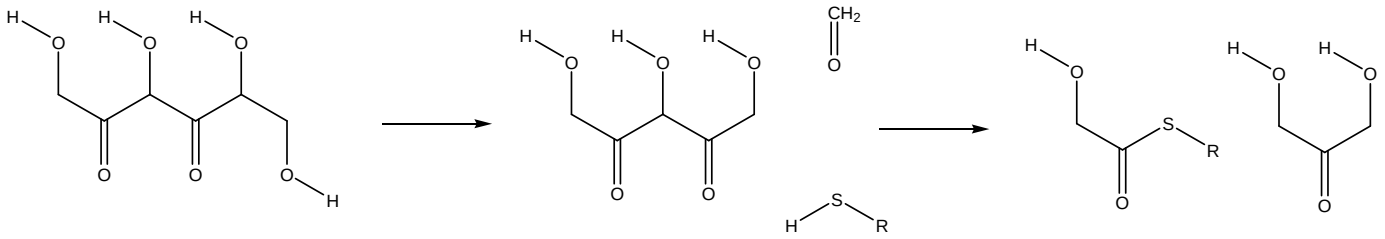

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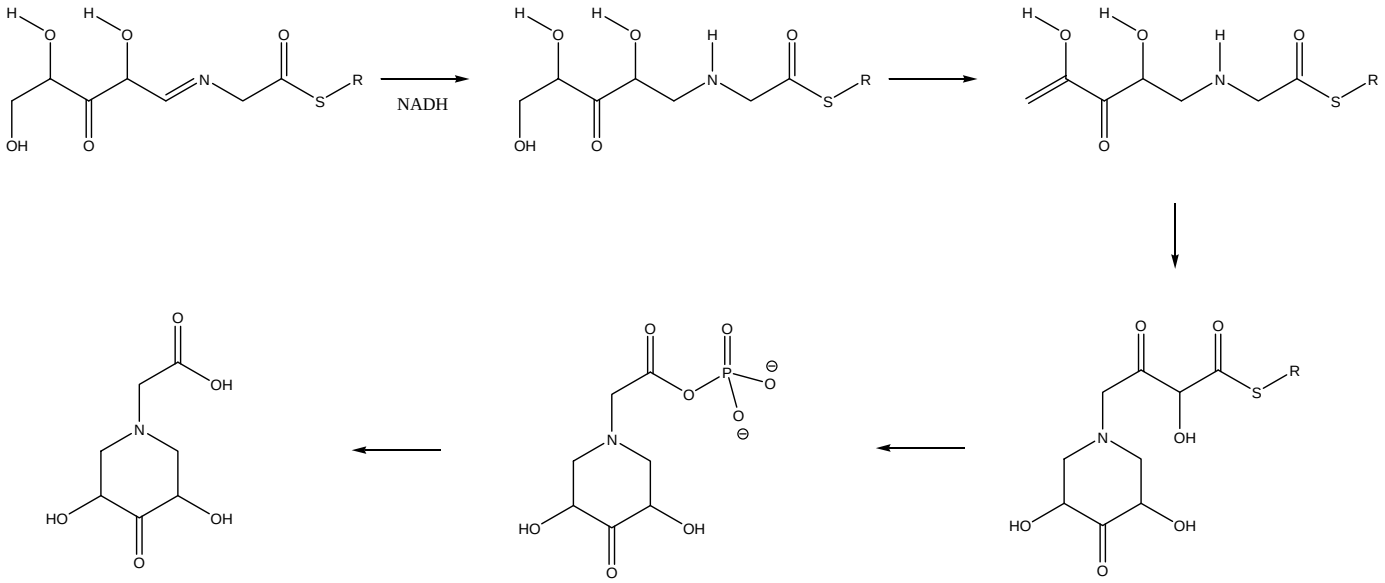

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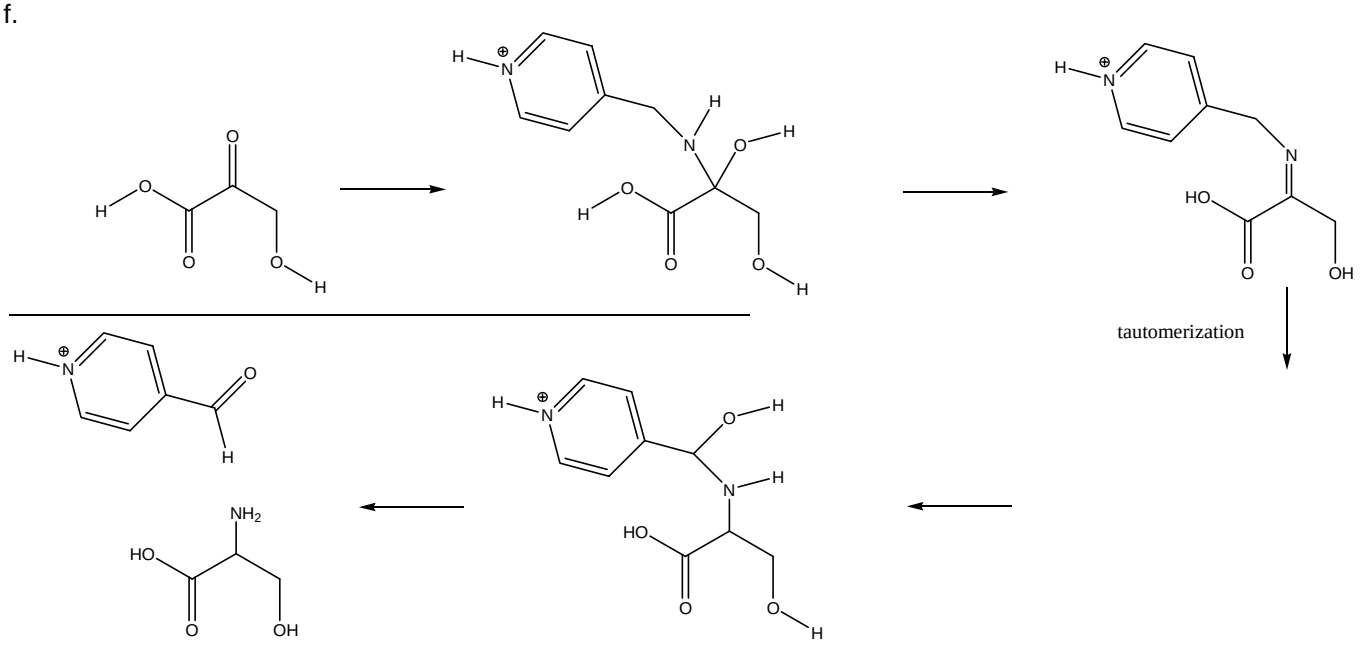
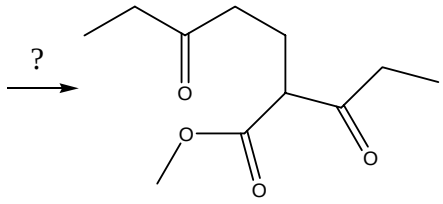
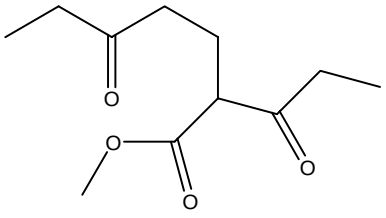
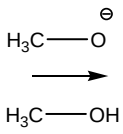


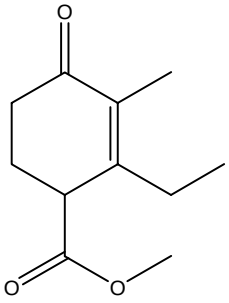
8. a. Provide the necessary starting materials and a complete arrow pushing mechanism to explain formation of the indicated product (show proper curved arrow conventions, lone pairs as two dots and single electrons as one dot). You only need to show the most important resonance structure and (←→ Res.) whenever resonance is present. The necessary starting structures will be supplied for 3 points (12 pts)



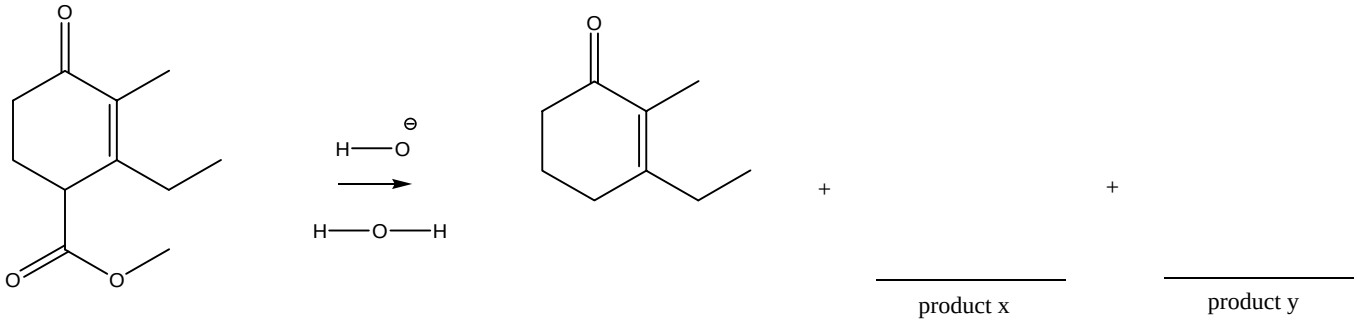
b. Provide a detailed mechanism for the next step of the synthesis. You only need to show the most important resonance structure and (←→ Res.) whenever resonance is present. (8 pts)



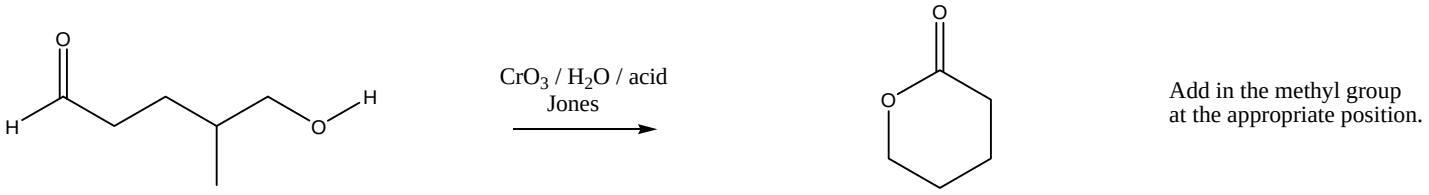




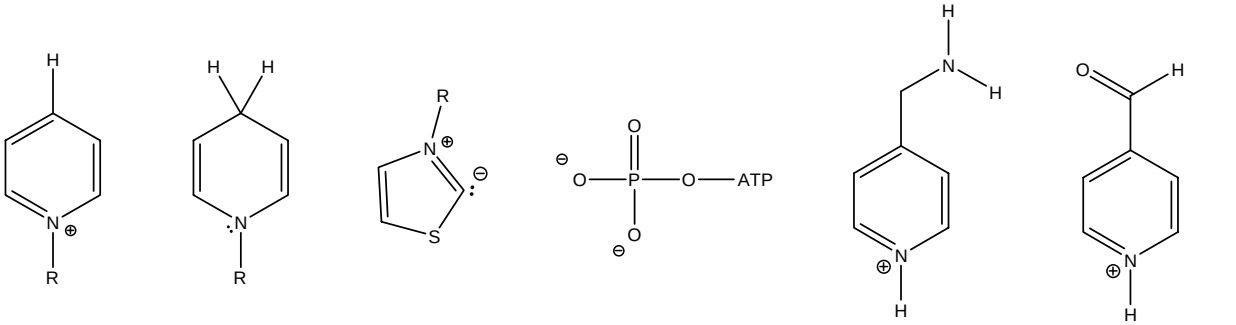
c. Provide a detailed mechanism for the next step of the synthesis. You only need to show the most important resonance structure and (←→ Res.) whenever resonance is present. Indicate what products x and y are. (10 pts)



9. Propose a complete arrow pushing mechanism for the following reaction from the tetradotoxin synthesis. Hint: Make a hemi-acetal first, using the acid, and then do the usual Jones CrO_3 reaction. (15 pts)



Simplified co-factors for the bio-organic game problems, if needed.



NAD^+ equivalent | NADH equivalent | TPP ylid | ATP | vitamin B-6 (1^o amine version) | vitamin B-6 (aldehyde version)

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No person is free who is not master of himself. Epictetus

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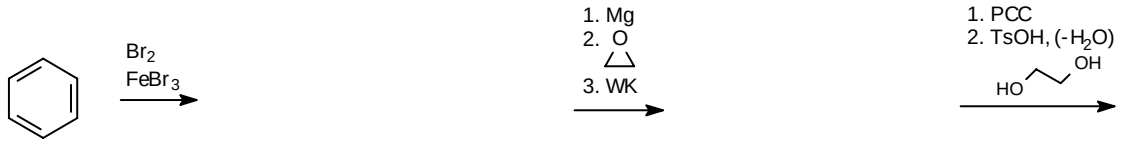
a.



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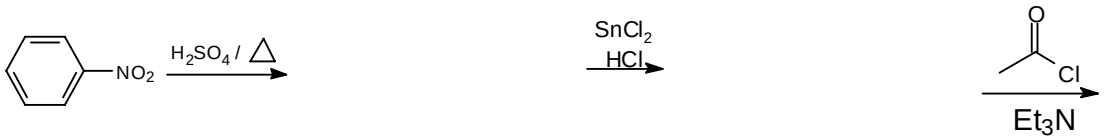

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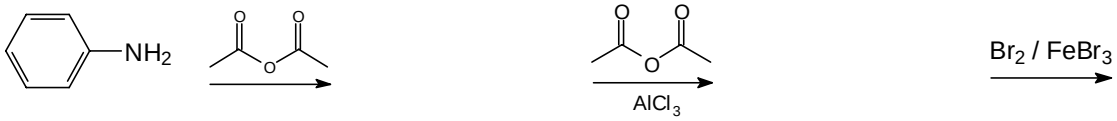

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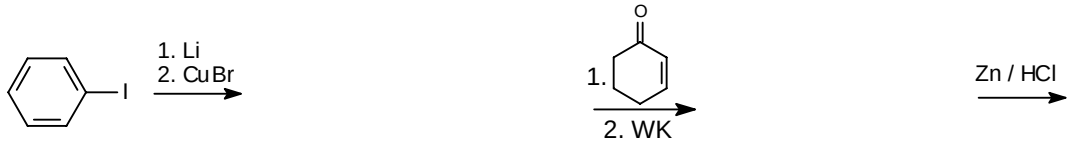

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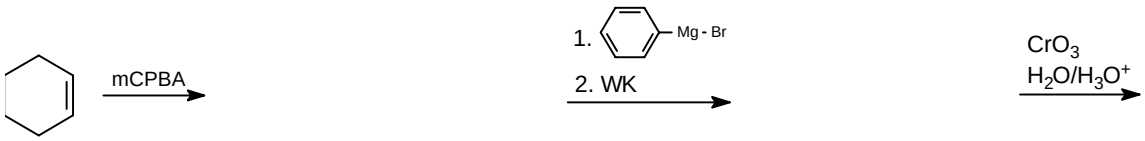

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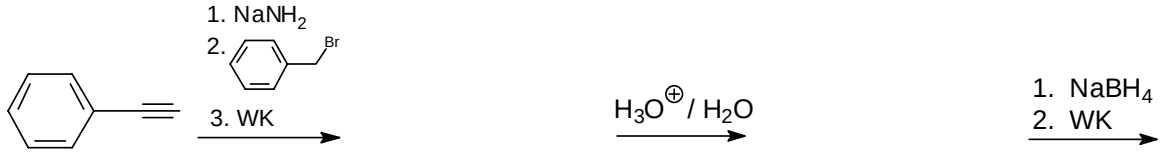

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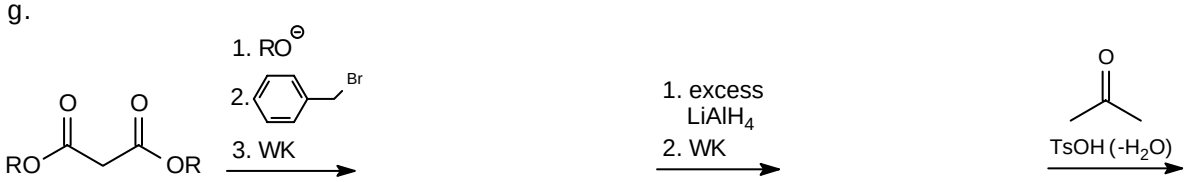

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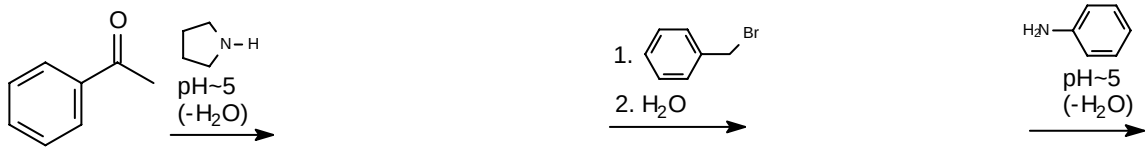

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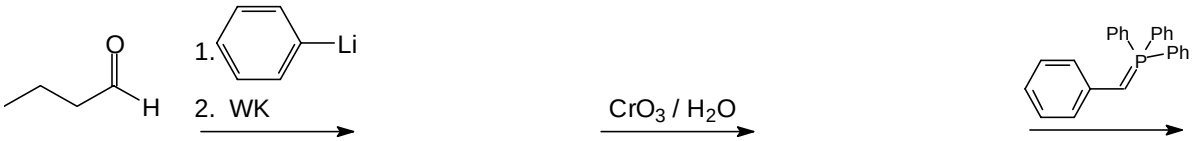

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