California State Polytechnic University, Pomona

Chem 316
Final Exam
Winter, 2009
Beauchamp

Name: _____

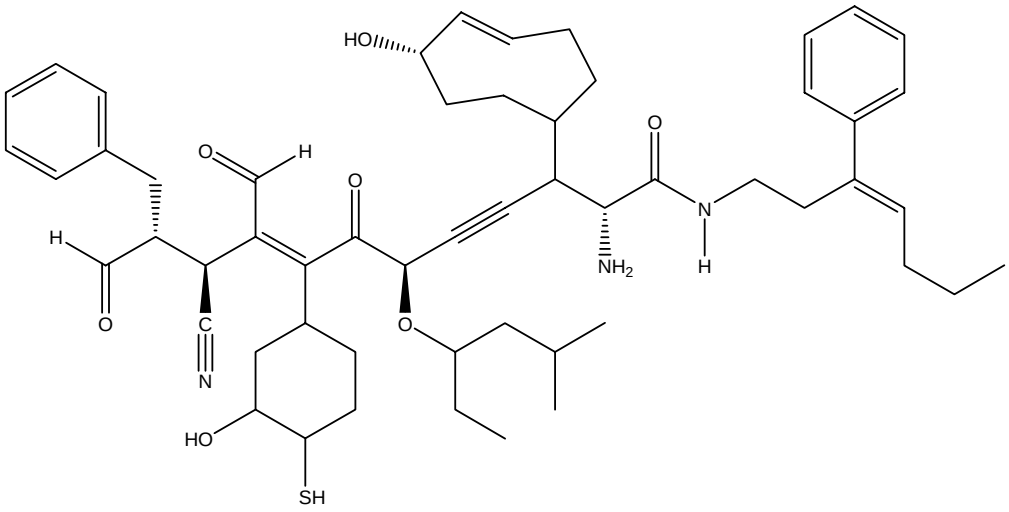
Topic	Total Points Exam Points	Credit
1. Nomenclature (1)	30	
2. Explanation of Relative Reactivities of Aromatic Compounds or Carbonyl Compounds	24	
3. Reactions Page (10 x 3 = 30)	30	
4. Aromatic Mechanism and Explanation of Substituent Effects	38	
5. Tautomers (acidic conditions and base conditions)	30	
6. C-14 Synthesis	30	
7. Bio-organic Game (reaction recognition/simplistic mechanisms)	52	
8. Two Organic Mechanisms from Tetradotoxin Synthesis	30	
Total	264	

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.

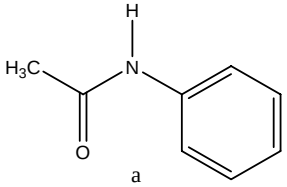
The cure for boredom is curiosity. There is no cure for curiosity. Dorothy Parker

California State Polytechnic University, Pomona

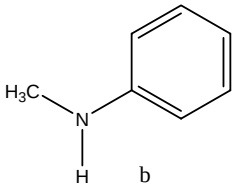
1. Provide an acceptable name for the following structure. (30 pts)



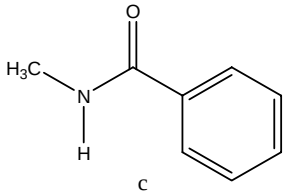
2. State whether each of the following aromatic substituents acts as an activating or deactivating group on the aromatic ring. Order the substituents in decreasing order of activating influence on the aromatic ring (*1 = most activating*). Show *some* intermediate structures that will explain your order of reactivity. Write out the reaction conditions for bromination and an expected *major* product in each case. (24 pts)



a



b

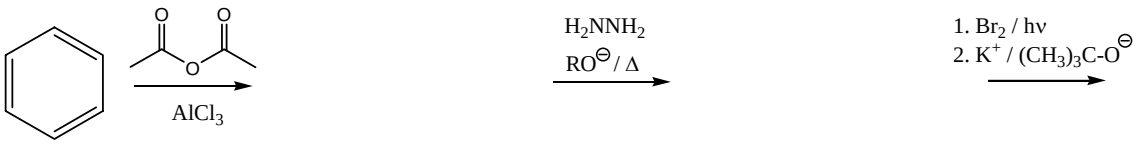


c

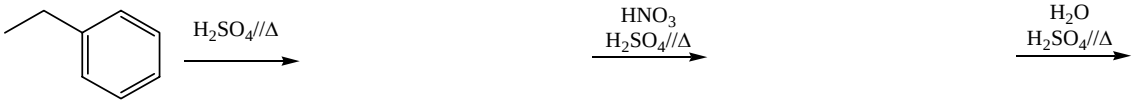
California State Polytechnic University, Pomona

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)

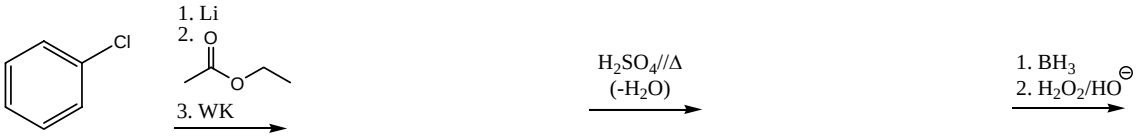
a.



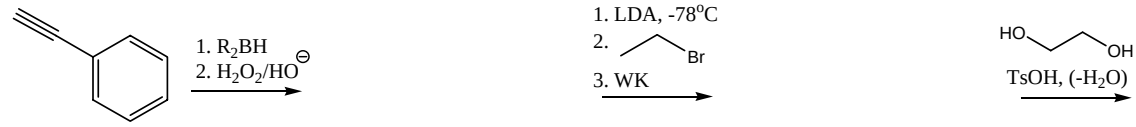
b.



c.

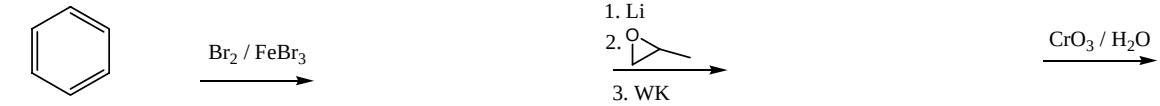


d.

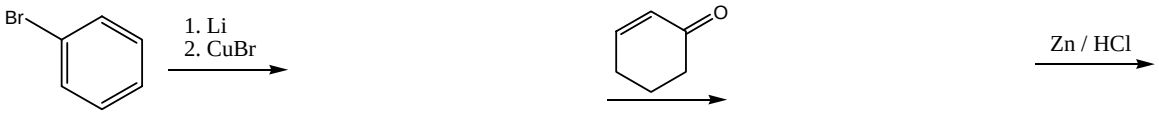


e.

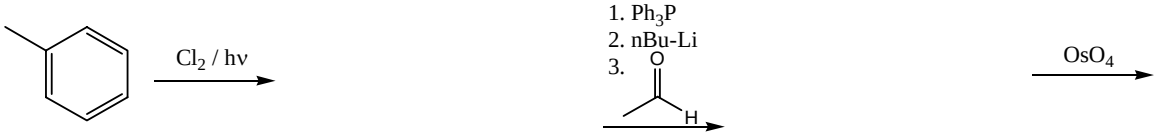
f.



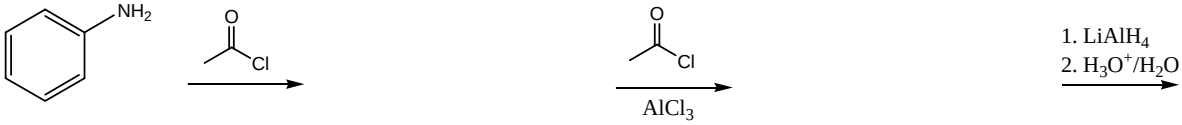
g.



h.

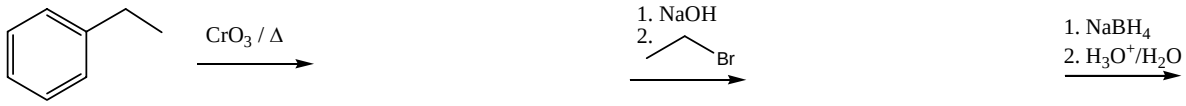


i.



j.

California State Polytechnic University, Pomona



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. (10 pts)

i.

ii.

b. Provide mechanisms that show how any necessary **<u>electrophiles</u>** reacting with the aromatic ring are generated. (8 pts)

i.

ii.

c. Provide a mechanistic explanation that explains the observed regioselectivity (*ortho*/*para*, or *meta*) when the *second electrophilic group* adds to the aromatic ring in each of your proposed syntheses in part a. You do not have to show every resonance structure, just enough to explain the observed regioselectivity. (20 pts)

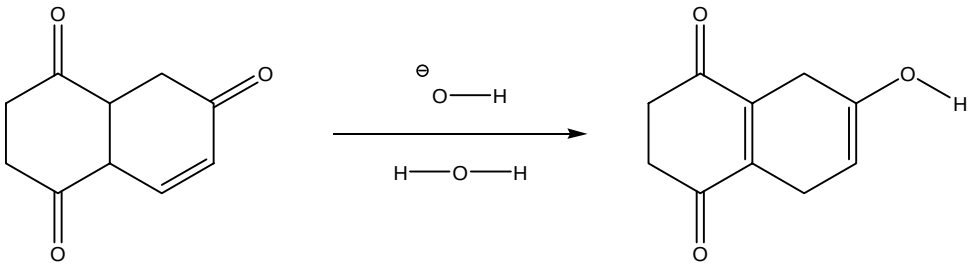
i.

ii.

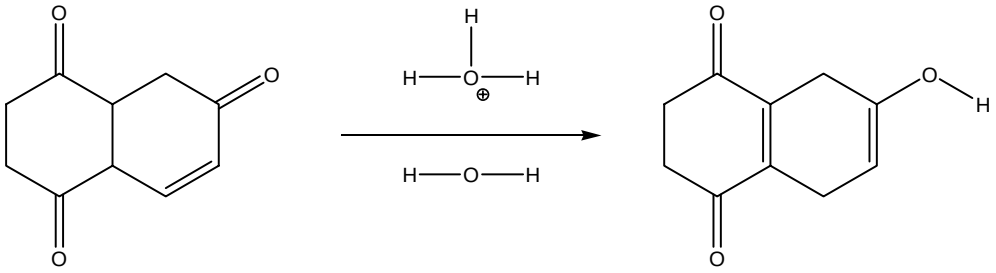
California State Polytechnic University, Pomona

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 = 30 pts)

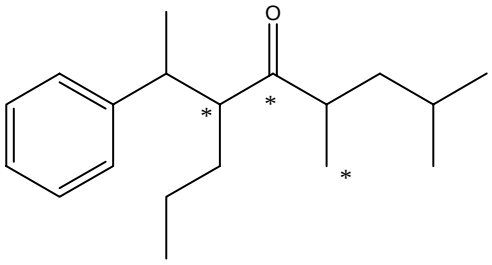
a.



b.

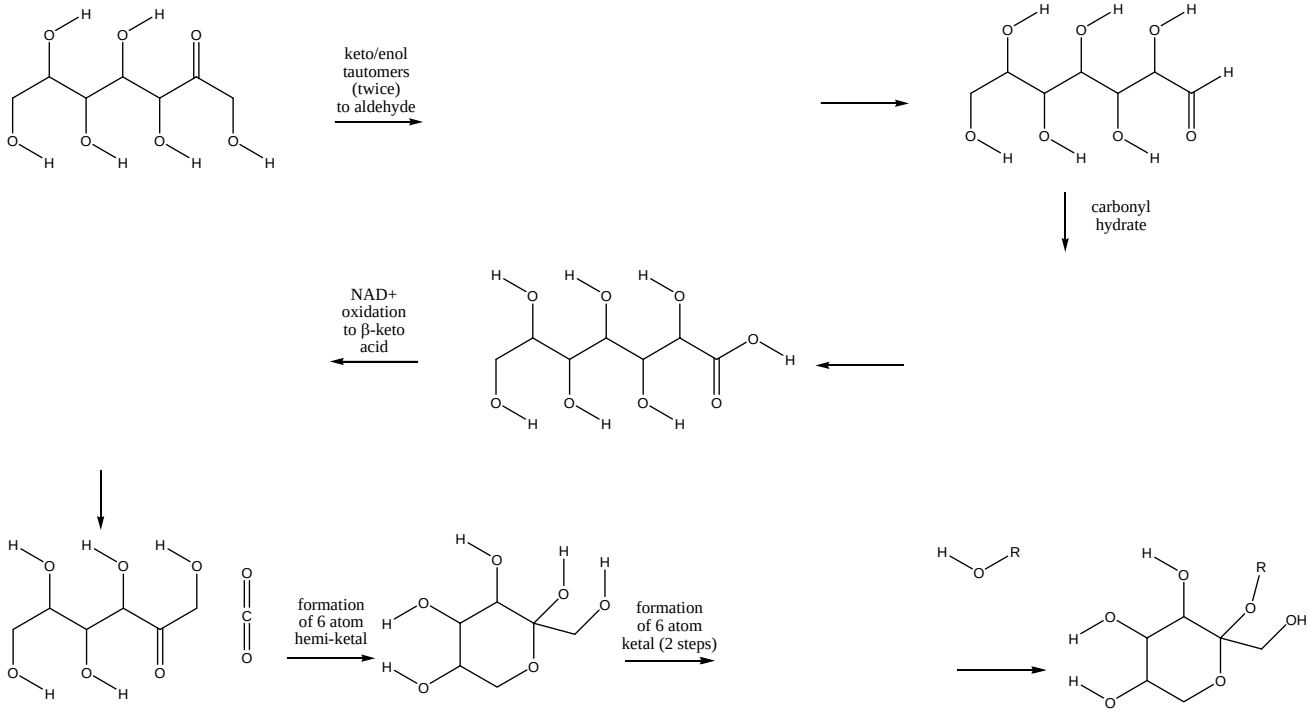


6. Propose a synthesis for the following compound using methane, ethane, propane, cyclohexane, benzene, sodium cyanide and/or carbon dioxide. Your only sources of radioactive ^{14}C carbon are methane, $*CH_4$, carbon dioxide, $*CO_2$ and sodium cyanide, Na*CN. You may also use any typical organic reagents. 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)

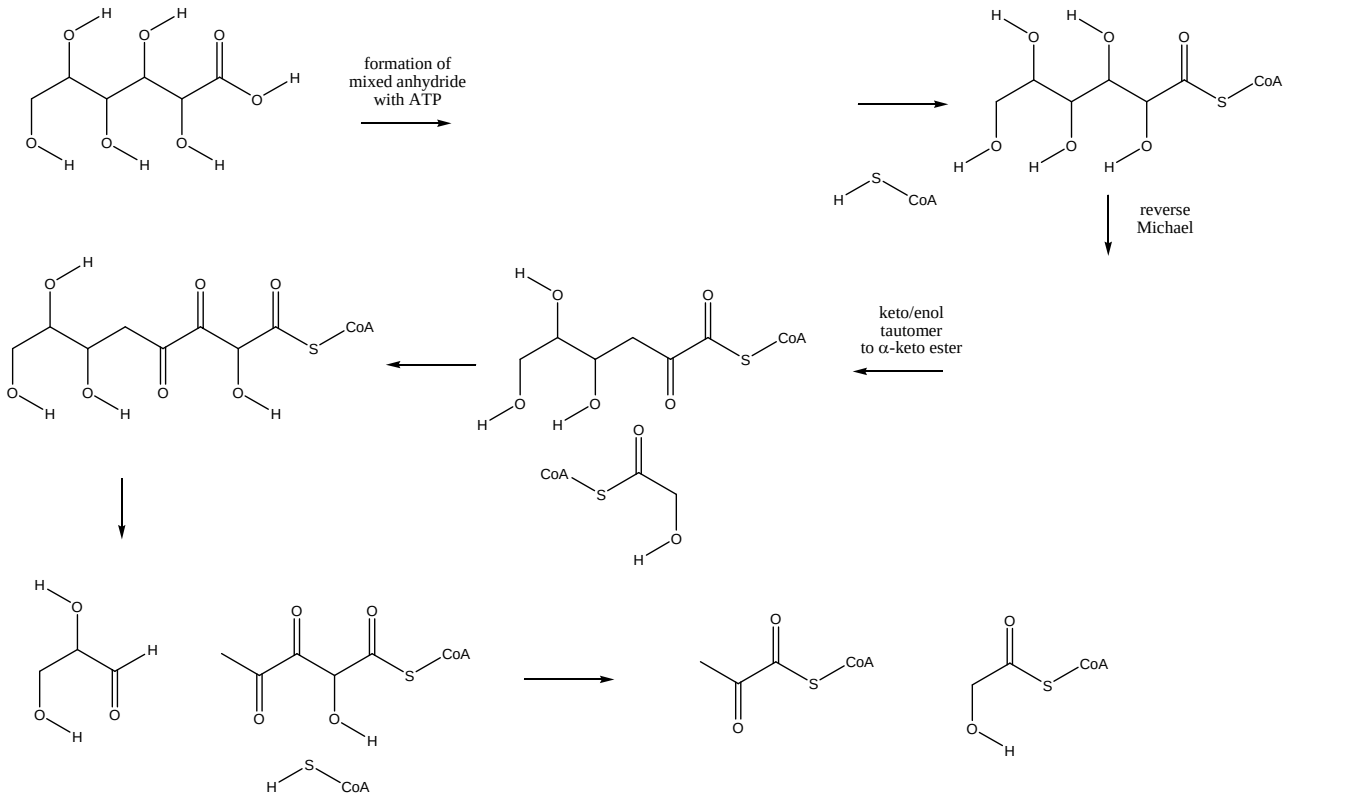


7. From the given bio-organic structure, use our simplistic mechanisms to show how each transformation could occur. If any structures are missing, use the descriptive term to fill in the necessary structures and details. Draw in any additional atoms or structures needed to demonstrate the transformations (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.** (52 pts)

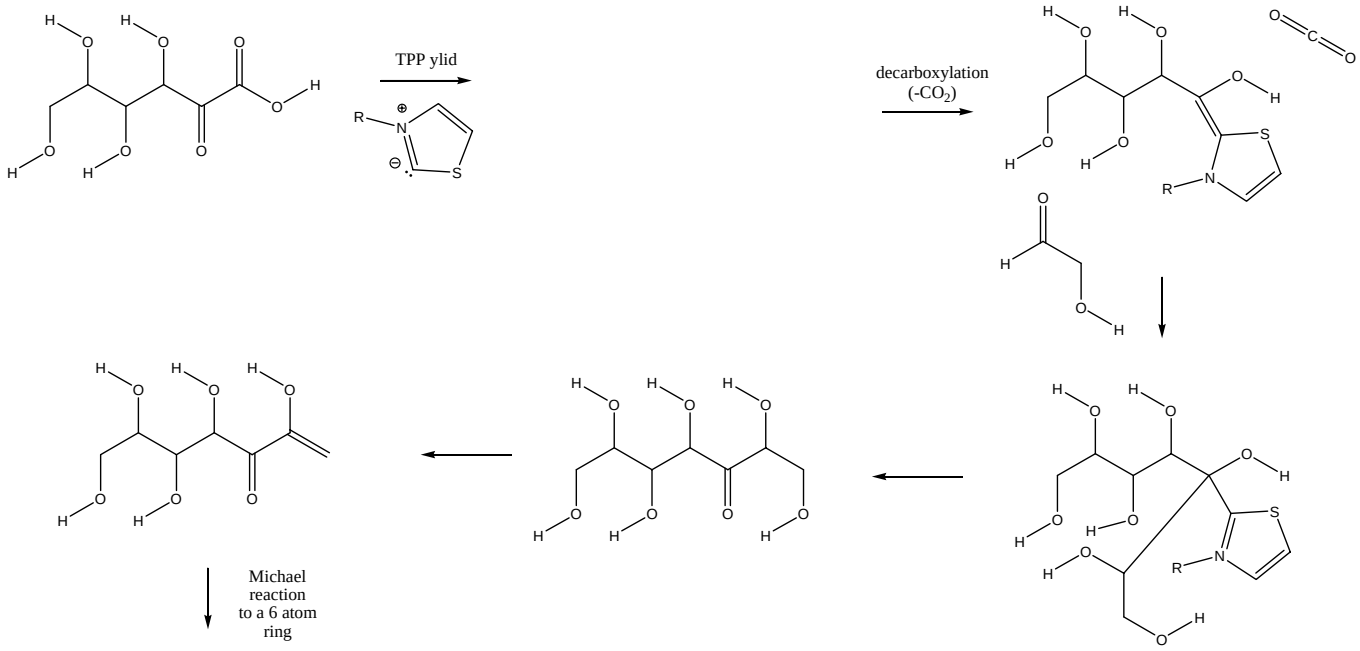
a.



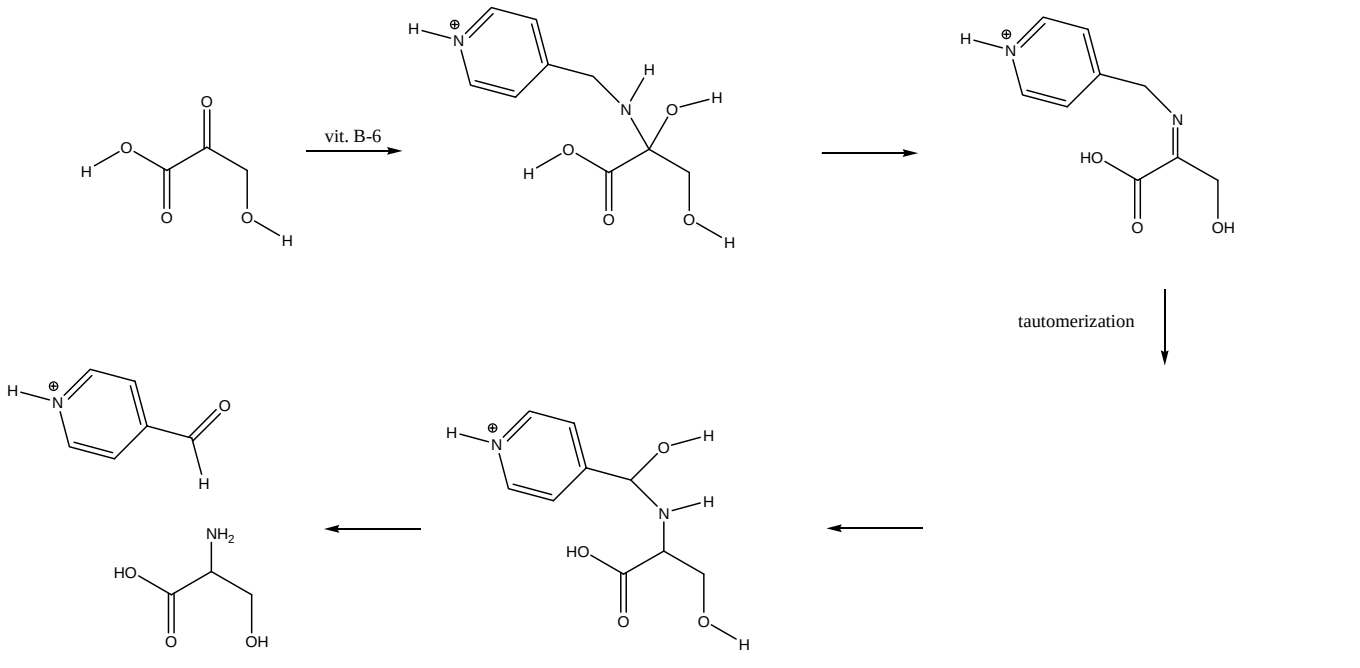
b



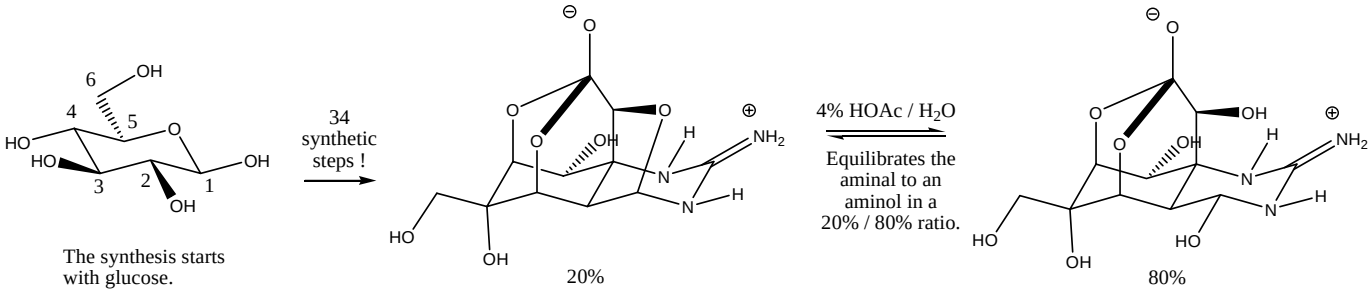
c.


TPP ylid
decarboxylation
(-CO2)
Michael
reaction
to a 6 atom
ring

d.


vit. B-6
tautomerization

8. Two steps were chosen from a 34 step synthesis of tetrodotoxin to ask two simplified organic mechanisms. The structures have been simplified to make it more reasonable to propose a complete arrow-pushing mechanism (lone pairs, formal charge and curved arrows). Use your organic logic, learned over the past year, to propose a reasonable organic mechanism. (30 pts)



The synthesis starts with glucose.

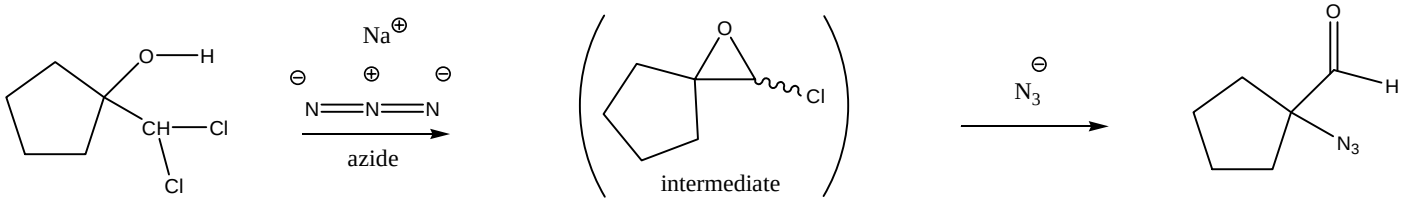
20%

80%

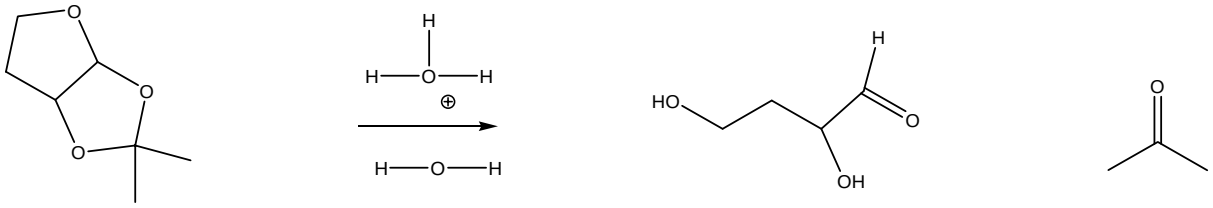
Tetradotoxin is the extremely poisonous puffer fish toxin. The overall yield of 34 steps in this synthesis is 0.38 %. That's an average yield of about 85% per step overall.

---

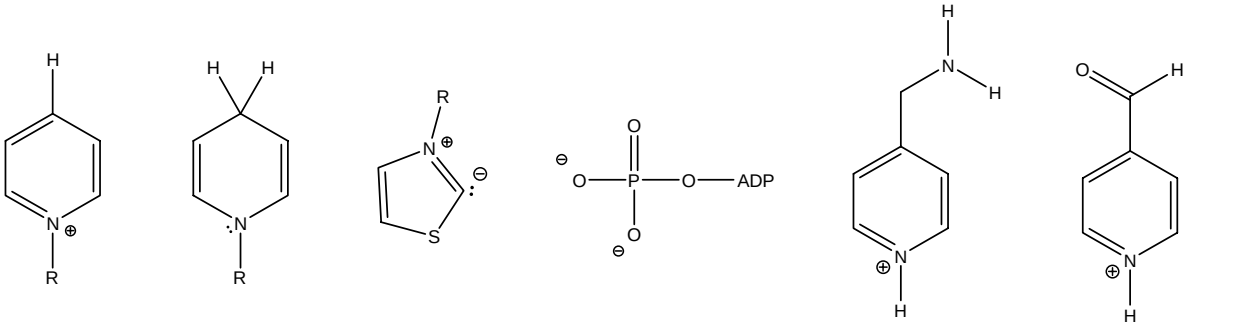
a. Use azide (N_3^-) as a base, and then as a nucleophile. The first step is similar to the way we first made epoxides. After that, look where the nuclephilic azide ends up and finish the reaction. (15 pts)



b. Number your carbons to help you see how each one ends up. Use H_3O^+/H_2O to show your mechanism.



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)

California State Polytechnic University, Pomona

After climbing a great hill, one only finds that there are many more hills to climb. Nelson Mandela