California State Polytechnic University, Pomona

Chem 316
Midterm Exam
Spring, 2004
Beauchamp

Name: _____

Topic	Total Points Exam Points	Credit
1. Nomenclature (1)	25	
2. Tautomers (in acid and in base)	24	
3. Short syntheses using reactions learned thus far (8)	64	
4. C-14 synthesis (methanol, ethanol, cyclohexene, propene bromobenzene, NaCN, CO_2, C-14 compounds)	25	
5. Carbohydrate Game (reaction recognition/simplistic mechanisms	28	
6. Arrow-pushing Mechanisms, one in acid and one in base	40	
Total	206	

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.

We must learn to live together as brothers and sisters...or perish together as fools.

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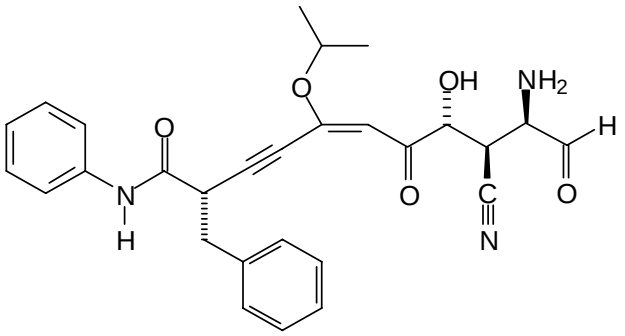
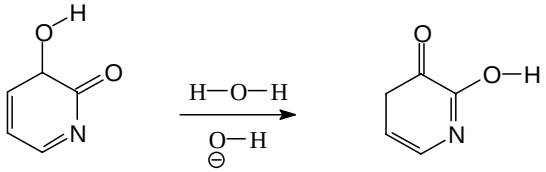
1. Provide an acceptable name for the following structure. (25 pts)

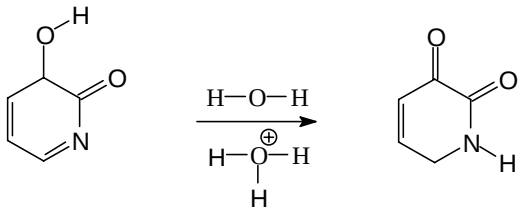


2. Provide complete arrow-pushing mechanisms for each reaction below. Include curved arrows, lone pairs of electrons and formal charge. If resonance is present, draw at least one additional resonance structure to show you recognize this feature (make sure the "best" resonance structure is included in your two resonance structures). (24 pts)

a.



b.



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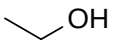
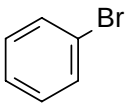
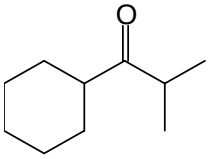
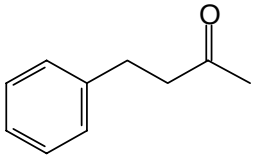
3. In each part below you are given a target and a starting molecule. If no additional information is provided, you may propose any synthesis that is reasonable to work your way back to a given starting compound. If a particular approach is specified you must meet those conditions, as well (e.g. use cyanide, use an aldol reaction, use a Wittig reaction, etc.). You may use any typical reagents available in our course. Your sources of carbon for the target structures include any given starting compound and the "allowed sources of carbon" shown below. If you synthesize a molecule in one part you can refer back to that part to use it again in another part. 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. (64 pts)

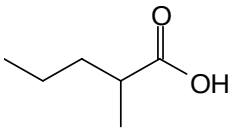
Allowed sources of carbon to incorporate into target molecules (besides any given starting compounds).

CH_3OH    NaCN CO_2 

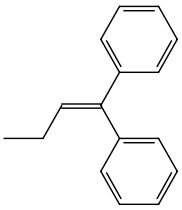
a. Target  Requirements: Use a nitrile in the synthesis

b. Target  Requirements: Use dithiane in the synthesis

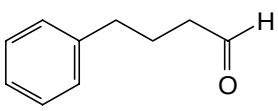
c. Target Requirements: Use a dianion in the synthesis



d. Target Requirements: Use an ester in the synthesis



e. Target Requirements: Use an alkyne in the synthesis



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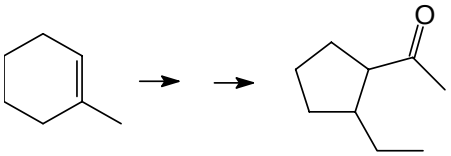
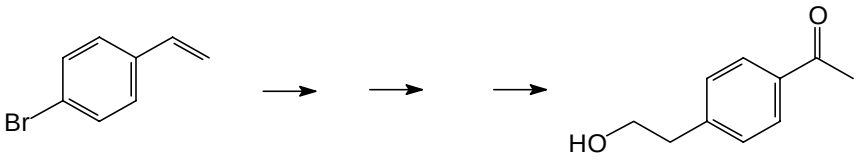
f. Target Requirements: Use a Claisen reaction, acetoacetic ester and a dianion in the synthesis

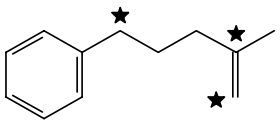
g. Target Requirements: Use the given alkene, ozonolysis, an aldol and a cuprate in the synthesis



h. Target Requirements: Use the given structure and protection in the synthesis.

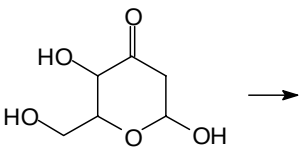


4. Propose a synthesis for the following compound using methanol, ethanol, propene, cyclohexene, bromobenzene, sodium cyanide or carbon dioxide. Your only source of radioactive C-14 carbon is C-14 methanol, $*CH_3OH$, carbon dioxide, $*CO_2$ and sodium cyanide, Na*CN. You may also use any typical organic 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. (25 pts)

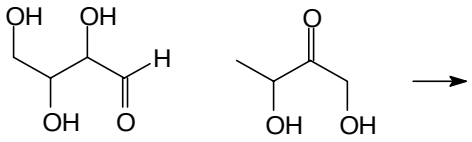


5. From the given carbohydrate, use a simplistic nondetailed mechanism to show how each transformation could occur. Add in any additional atoms to demonstrate your transformations. Use B: if you need a base and $B\text{-}H^{\oplus}$ if you need an acid. (28 pts)

   a. reverse Michael reaction to open the ring, followed by keto/enol tautomerization to form an aldehyde

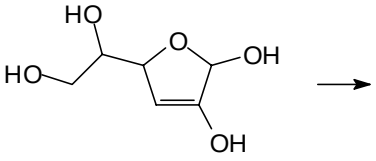


b. aldol to a straight chain C_8 structure, followed by hemiketal formation to a 6 atom ring



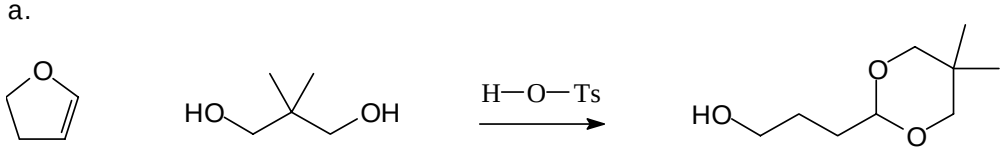
c. retro-aldol followed by an aldol forming the given structure

d. retro-hemiacetal reaction, followed by a Michael reaction using a water molecule

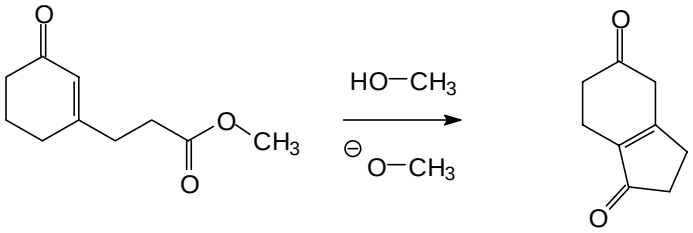


5. Provide complete arrow-pushing mechanisms for each reaction below. Include curved arrows, lone pairs of electrons and formal charge. If resonance is present, draw at least one additional resonance structure to show you recognize this feature (make sure the "best" resonance structure is one of your two resonance structures). (40 pts)

a.



b.



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An example of possibilities in synthesis problems (there may be others not listed below…?)

1. use an acid chloride
2. use a carboxylic acid
3. use a nitrile
4. use an alcohol and oxidation
5. use dithiane
6. use ozonolysis
7. use cuprates
8. use Mg or Li in reaction
9. use an alkyne
10. use an ester
11. use acetoacetic ester
12. use malonic diester
13. use DIBAL
14. use the Wittig reaction
15. use the Michael reaction
16. use the Robinson annelation
17. use dianions
18. use protection
19. use phthalimide
20. use reduction
21. use a diol
22. use an epoxide
23. use cyanide or carbon dioxide
24. use an aldol reaction
25. use a Claisen reaction

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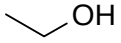
Preview of Exam Questions (handout before the exam)

1. Provide an acceptable name for the following structure. (20 pts)

2. Provide complete arrow-pushing mechanisms 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. Conjugate addition and tautomerism are parts of these problems. (30 pts)

3. In each part below you are given a target and a starting molecule. If no additional information is provided, you may propose any synthesis that is reasonable to work your way back to a given starting compound. If a particular approach is specified you must meet those conditions, as well (e.g. use cyanide, use an aldol reaction, use a Wittig reaction, etc.). You may use any typical reagents available in our course. Your sources of carbon for the target structures include any given starting compound and the "allowed sources of carbon" shown below. 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. (56 pts)

   Allowed sources of carbon to incorporate into target molecules (besides any given starting compounds).

   CH_3OH    NaCN CO_2

4. Propose a synthesis for the following compound using methanol, ethanol, propene, cyclohexene, bromobenzene, sodium cyanide or carbon dioxide. Your only source of radioactive C-14 carbon is C-14 methanol, $*CH_3OH$ 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. (20 pts)

5. From the given carbohydrate, use a simplistic nondetailed mechanism to show how each transformation could occur. Add in any additional atoms to demonstrate your transformations. Use B: if you need a base and B-H$^{\oplus}$ if you need an acid. (20 pts)

6. Predict trends and provide an mechanistic explanation. (20 pts)

7. Provide complete arrow-pushing mechanisms 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.
   Two parts: one in acid and one in base. (30 pts)