Chem 315 Final Exam Winter, 2012 Beauchamp

Торіс	Total Points Exam Points	Credit
1. Nomenclature (1)	30	
2. Five Short Syntheses or Compare Relative Reactivities	20	
3. Reactions Page, using reactions learned thus far (30)	30	
4. Mechanisms using acid and base (3 at 12 pts each)	36	
5. Tautomers (in acid and in base) (2 at 12 pts each)	24	
6. Synthesis (3 target molecules, including ¹⁴ C, 3 at 15 pts each)	45	
7. S _N 1/E1 and S _N 2/E2 reaction details. Stereochemistry, Arrow Pushing, Carbocations, Rearrangements	32	
8. Alkene Reactions (predict products with regioselect., stereoselect. details)	36	
Total	253	

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. You get points for writing correct information. You do not get any points for writing wrong information or blank pages. Make sure you show all of your work. Draw in any lone pairs of electrons, formal charge and curved arrows to show electron movement in mechanism and explanation problems. If resonance is part of an answer, draw the best resonance structure, plus at least one additional resonance structure to show that resonance is present. Only write answers on the front of each page. Do your best to show me what you know in the time available.

The important thing is this: To be able at any moment to sacrifice what we are for what we could become. - Charles DuBois

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

2. Predict the relative order of reactivity of the indicated carbonyl compounds in reactions with nucleophiles (1 = most reactive carbonyl electrophile). Use all three routine arguments of organic chemistry (resonance, inductive and steric). Show structures, lone pairs and arrow-pushing conventions in your answer to provide an explanation for your order of reactivity. For B, C and D write the expected product in a reaction with lithium aluminium deuteride, LiAlD₄, followed by workup. (20 pts)

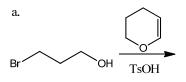
A CH₃

O

c o

 $\begin{array}{c|c} & & & \\ & & & \\ & & & \\ \end{array}$

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



Cu

$$\ominus$$

 Li^{\oplus}

$$K_{\Theta}$$

$$H_2C \longrightarrow P(Ph)_3$$

i.
$$OOO$$
 OH OH $TsOH (-H_2O)$

j. 1 eq. OH HO
$$\longrightarrow$$
 TsOH (-H₂O)

3. Provide a complete arrow-pushing mechanism (curved arrows, lone pairs and formal charge) to explain the following transformations. If resonance structures are present, show the "best" one, and at least one other resonance structure to demonstrate that you are aware of its presence. Make sure to take account of the acid or base conditions. (36 pts, a, b, c = 12 pts each)

a.

Explain why the reaction occurs this way and not any other possible ways.

b.

Two different bridging intermediates. Hint: there are 2 oxygen atoms in acetate (which could form a bridge) and the stereochemistry in the product is trans.

NaOH
H₂O
Only show a mechanism for one of the acetates reacting.

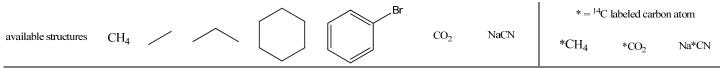
5. Provide a complete arrow-pushing mechanism for the following transformations (curved arrows, lone pairs, formal charge and at least 2 resonance structures, including the "best" one). Restrict your tautomeric changes to keto or enol portions of the molecules, not isolated carbon-carbon double bonds. (24 pts) a. (12 pts)

$$0 \longrightarrow H \longrightarrow H$$

$$0 \longrightarrow H \longrightarrow H$$

$$0 \longrightarrow H \longrightarrow H$$

6. Propose a reasonable synthesis for the following molecule. Allowed starting carbon structures are shown below. You may also use any other routine reagents discussed in our course. Begin at the end, with the given structure, and work backwards to allowable starting materials. You must show the reagents and starting structure for each step of your synthesis. Do NOT show mechanisms. (45 pts, 15 pts each)



a. *

Target Molecule 1 (15 pts)
Hint: cuprate and Wittig
reactions might prove helpful.

Target Molecule 3 (15 pts)

7. Write the structure(s) of the expected **major** product(s). Include a simple mechanism that clearly shows how the reaction likely proceeds. State what mechanism each reaction follows. If chiral centers are present, indicate absolute configuration(s). Show 3D representations when necessary to explain the result. If rearrangements are reasonable, assume they will happen. (32 pts)

H—O—SO₃H

$$\Delta$$
(show a mechanism for the major product and draw all other expected products)

$$H_3C$$
 H
 D
 H
 D
 H
 D

8. Using the given alkenes, show the expected stereochemical and regiochemical result for each set of conditions in 3D. State whether the products will reveal if the reaction is stereoselective and/or regioselective. Also indicate whether the product(s) is(are) chiral, enantiomers, diastereomers, meso or no chiral centers. If more than one product is formed, predict which is the major product or if they are formed in equal amounts. In column A classify all chiral centers as R or S. (36 pts)

in equal amounts	. In column A classify an cm	ral centers as R or S. (36 pts)	
Alkenes	H_3C C D H		M _{Mm}
Reagent 1 1. BD ₃ ⊖ 2. H ₂ O ₂ , HO			
2. H ₂ U ₂ , HU →			
Reagent 2			
1. mCPBA 2. CH ₃ O [⊖] , CH ₃ OH			

Men are not prisoners of fate, but only prisoners of their own minds. - Franklin D. Roosevelt

Preview of Exam Questions

- 1. Provide an acceptable name for the given structure. (25 pts)
- 2. Predict the relative order of reactivity of strong nucleophiles to the indicated carbonyl compounds (1 = most). Provide an explanation for that order of reactivity. Use all three routine arguments of organic chemistry. Show structures, lone pairs and arrow-pushing conventions in your answer. Write out the expected products for the addition of "X" to each carbonyl center after acidic workup? You do not need to show mechanisms. (20 pts)
- 3. Provide the expected product for each of the following reactions. Show regiochemistry and stereochemistry clearly, if relevant. Do NOT show mechanisms. WK = workup (45 pts)
- 4. Provide a complete arrow-pushing mechanism (curved arrows, lone pairs and formal charge) to explain the given transformations (one in acid and one in base). If resonance structures are present, show the "best" resonance structure and at least one other resonance structure to demonstrate that you are aware of their presence. Make sure to take account of the acid or base conditions. (24 pts)
- 5. a and b. Provide a complete arrow-pushing mechanism (curved arrows, lone pairs, formal charge, important resonance structures) for the tautomeric transformations (one in acid and one in base). Restrict your tautomeric changes to keto or enol portions of the molecules, not isolated carboncarbon double bonds. If oxygen is part of an anionic or cationic resonance system, show that structure. (24 pts)
 - c. Write out 5 additional tautomeric structures different than those drawn above (there are several more possible). Remember the number of π bonds and the formal charge does not change among tautomers. (5 pts)
- 6. Propose a reasonable synthesis for the given molecule. Your only source of ¹⁴C is labeled methane, *CH₄, carbon dioxide, *CO₂, and Na*CN. You may also use non-¹⁴C methane, ethane, propane, bromobenzene, NaCN and CO₂ as well as any other routine reagents discussed in our course. Begin at the end, with the given structure, and work backwards to allowable starting materials. You must show the reagents and starting structure for each step of your synthesis. Do NOT show mechanisms. (30 pts)
- 7. Write the structure(s) of the expected **major** product(s). Include a simple mechanism that clearly shows how the reaction likely proceeds. State what mechanism each reaction follows. If chiral centers are present, indicate absolute configuration(s). Show 3D representations when necessary to explain the result. If rearrangements are reasonable, assume they will happen. (28 pts)
- 8. Using the given alkenes, show the expected stereochemical and regiochemical result for each set of conditions. State whether the products will reveal if the reaction is stereoselective and/or regioselective. Also indicate whether the product(s) is(are) chiral, enantiomers, diastereomers, meso or no chiral centers. If more than one product is formed, predict which is the major product or if they are formed in equal amounts. In column A classify all chiral centers as R or S. (30 pts)

4. Propose a series of synthetic steps that will transform the indicated starting material into the target molecule. You can use any other reagents and molecules you need (you don't need to make them). Each part can be done in as few as 3 steps. This should take 3-4 synthetic steps. Do not show mechanisms (30 pts)

