Chem 315 Final Exam Fall, 2006 Beauchamp

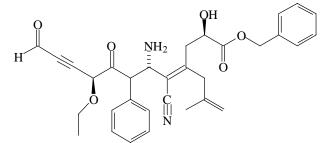
Name: \_\_\_\_\_

Торіс	Total Points Exam Points	Credit
1. Nomenclature (1)	25	
2. Relative Order of Reactivity	20	
3. Reactions Page, using reactions learned thus far (30)	45	
4. Mechanism in acid and mechanism in base	24	
5. Tautomers (in acid and in base) and Drawing Additional Tautomer Structures.	29	
6. <sup>14</sup> C Synthesis	30	
<ol> <li>S<sub>N</sub>1/E1 and S<sub>N</sub>2/E2 reactions. Stereochemistry, Arrow Pushing, Carbocations, Rearrangements</li> </ol>	24	
8. Alkene Reactions (Regioselect., Stereoselect.)	30	
Total	227	

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 <u>of your work</u>. 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.

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

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



 Predict the relative order of reactivity of strong nucleophiles with the indicated carbonyl compounds (1 = most reactive). Provide an explanation for your 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 reaction of ethyl lithium to carbonyl compounds B, C and D, after acidic workup? You do NOT need to show mechanisms. (20 pts)



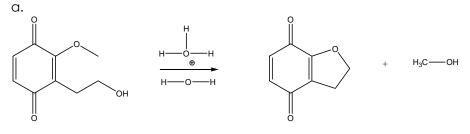
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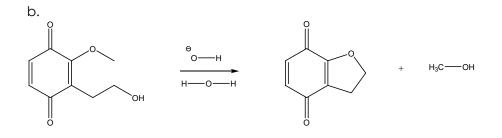
Expected products for B, C and D with ethyl lithium, after workup.

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)

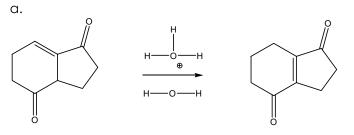
a.	$\begin{array}{c} 1. \text{ NaNH}_2/\text{NH}_3 \\ 2. \text{ CH}_2=\text{O} \\ 3. \text{ WK} \end{array}$	Pd/H <sub>2</sub> quinoline ►	1. NaH 2. $CH_3CH_2Cl$
b.	$\underbrace{\begin{array}{c}1.\text{ BH}_{3}\\2.\text{ H}_{2}\text{O}_{2}/\text{HO}\end{array}}_{\bullet}$	Jones CrO <sub>3</sub> /H <sub>2</sub> O	1. NaOH 2. CH₂=CHCH₂Br →
c.	$1. Br_2/hv$ $2. \qquad \bigcirc \\ \circ \\ \kappa^{\oplus}$	mCPBA	1. NaCN 2. WK →
d.	→OH SOCl <sub>2</sub>	1. Li 2. CH₃CH=O 3. WK	PBr <sub>3</sub>
e.	$1. \text{ Br}_2/\text{H}_2\text{O}$ 2. NaOH	$_{Na}^{\Theta}$	$\xrightarrow{Na, NH_3}$
f.	$ \begin{array}{c} 1. Mg \\ 2. CO_2 \\ 3. WK \end{array} $	1. SOCl <sub>2</sub> 2. $CH_3CH_2OH$	1. CH <sub>3</sub> Li 2. WK
g.	HO $H_2SO_4$	KMnO <sub>4</sub>	PCC
h.	$\underbrace{\begin{array}{c} 1. \text{ BH}_3 \\ 2. \text{ Br}_2/\text{ CH}_3\text{O} \end{array}}_{\bullet} \\ \bullet$	1. $()^{N\Theta}$ 2. Na OH	
i.	$ \underbrace{\begin{array}{c} 0 \\ 2. WK \end{array}}^{0} \underbrace{\begin{array}{c} 1. \text{ LiAlH}_4 \\ 2. WK \end{array}} $	Jones CrO <sub>3</sub> /H <sub>2</sub> O	$1. _{\text{Li}}$
j.	Br NaOH	1. Hg(OAc) <sub>2</sub> H <sub>2</sub> O 2. NaBH <sub>4</sub>	Ts-Cl

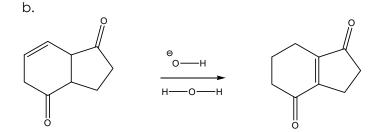
4. Provide a complete arrow-pushing mechanism (curved arrows, lone pairs and formal charge) to explain the following transformations. If resonance structures are present, show at least one other resonance structure to demonstrate that you are aware of their presence, including the "best" one. In neither example does the reaction begin with the methoxy group. Make sure to take account of the acid or base conditions. The base reaction is the simpler of the two mechanisms. (24 pts)





5. Provide a complete arrow-pushing mechanism for the following transformations (curved arrows, lone pairs, formal charge and <u>ALL</u> important resonance structures). Restrict your tautomeric changes to keto or enol portions of the molecules, not isolated carbon-carbon double bonds. If oxygen is part of an anionic or cationic resonance system, show that structure. (24 pts)



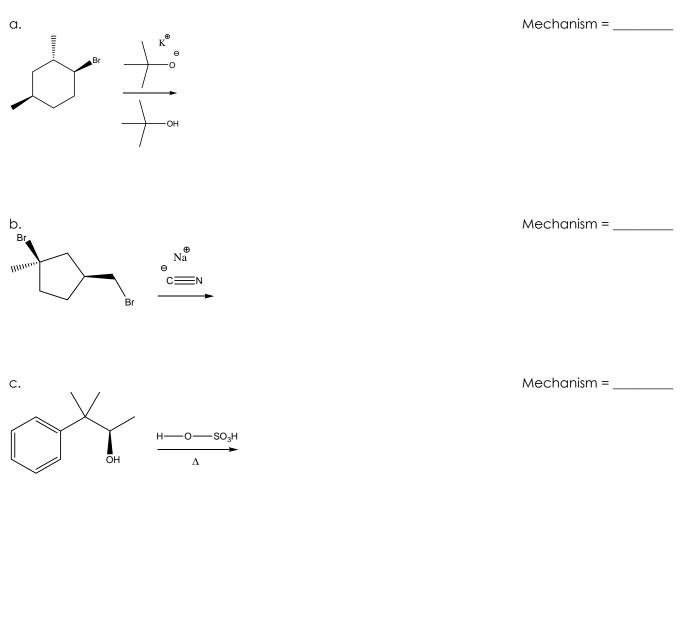


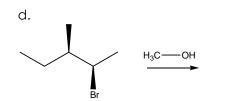
c. Write out 5 additional tautomeric structures **different** from those drawn above (there are many others possible). Remember the number of pi bonds and the formal charge does not change among tautomers. (5 pts)

1 2 3 4 5

6. Propose a reasonable synthesis for the following molecule. Your only source of <sup>14</sup>C is labeled methane, \*CH<sub>4</sub>, carbon dioxide, \*CO<sub>2</sub>, and Na\*CN. You may also use non-<sup>14</sup>C methane, ethane, propane, bromobenzene, NaCN and CO<sub>2</sub> 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)





Mechanism = \_\_\_\_\_

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)

Alkenes		
Reagent 1		
Reagent 2 Br2/CH3OH		

Preview of Exam Questions

- 1. Provide an acceptable name for the given structure. (25 pts)
- 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 carbon-carbon 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  $\pi$  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 <sup>14</sup>C is labeled methane, \*CH<sub>4</sub>, carbon dioxide, \*CO<sub>2</sub>, and Na\*CN. You may also use non-<sup>14</sup>C methane, ethane, propane, bromobenzene, NaCN and CO<sub>2</sub> 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)