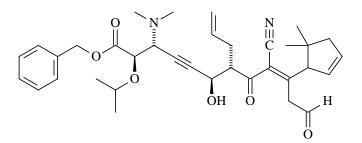
Chem 315 Final Exam Winter, 2004 Beauchamp

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

Торіс	Total Points Exam Points	Credit
1. Nomenclature (1)	25	
2. Mechanism and Relative Order of Reactivity	25	
3. Reactions Page, using reactions learned thus far (30)	30	
4. Mechanisms in base	26	
5. Tautomers (in acid and in base),	25	
6. <sup>14</sup> C Synthesis	27	
7. Carbonyl mechanism in acid	20	
8. S <sub>N</sub> 1/E1 and S <sub>N</sub> 2/E2 reactions. Stereochemistry, Arrow Pushing, Carbocations, Rearrangements	28	
9. Alkene Reactions (Regioselect., Stereoselect.)	28	
Total	234	

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

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



2. Both a ketone and a carboxylic acid will react with methanol under acid conditions. The ketone reacts with two methanol molecules, first in an addition reaction that is followed by an S<sub>N</sub>1 reaction. The carboxylic acid undergoes an acyl substitution at the carbonyl carbon. Provide a complete mechanism for both of the following reactions. Include all curved arrows, lone pairs and formal charge to show how the reaction proceeds. Also, draw a double headed arrow and write the word resonance whenever reasonable resonance structures exist. Specify which functional group is more reactive and provide a reason to explain your order. (25 pts, mechanism = 18 pts, explanation = 7 pts)

H<sub>3</sub>C-O O-CH<sub>3</sub> CH<sub>3</sub>- $CH_3 - O - H$ (remove H<sub>2</sub>O)

CH<sub>3</sub> OH OCH<sub>3</sub> CH<sub>3</sub>· (remove H<sub>2</sub>O)

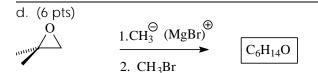
California State Polytechnic University, Pomona

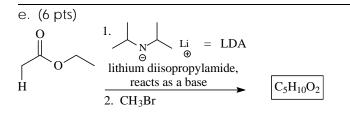
3. Provide the expected product for each of the following reactions. Show regiochemistry and stereochemistry clearly, if relevant. Do NOT show mechanisms. WK = workup (30 pts)

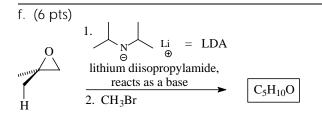
a.		ik – Wolkup (50 pts)
$Br_2$ $H_2O$	NaOH	$\underbrace{CH_{3}OH}_{CH_{3}OH_{2}} \oplus$
b.	Jones	1. CH <sub>3</sub> Li 2. WK
$\begin{array}{c c} & 2. \text{ H}_2 \text{O}_2/\text{HO}^{\Theta} \\ \hline \\ \text{C}. \end{array}$	1. excess $R_2 N^{\Theta}$	$3. H_2SO_4/\Delta$
$Br_2$	$\begin{array}{c} \text{R}_2\text{NH}\\ \text{2. CH}_3\text{Br}\\ \end{array}$	$\sim$ Na / NH <sub>3</sub>
$ \begin{array}{c}                                     $	1. O <sub>3</sub> / -78°C 2. CH <sub>3</sub> SCH <sub>3</sub>	1. CH <sub>3</sub> Li 2. WK 3. PBr <sub>3</sub> ►
$ \begin{array}{c} 1. \text{ Mg} \\ 1. \text{ Mg} \\ 2. \text{ o} \\ 1. \text{ Mg} \\$	PCC CrO <sub>3</sub> /no H <sub>2</sub> O	NH <sub>2</sub> TsOH (-H <sub>2</sub> O)
H H H	H <sub>2</sub> / Pd quinoline	$\frac{1. \text{ O}_3 / -78^{\circ}\text{C}}{2. \text{ NaBH}_4}$
Br h.	HO TSOH (-H <sub>2</sub> O)	1. Mg 2. CH <sub>2</sub> =O 3. $\underline{H_3O^+/H_2O}$
$ \begin{array}{c} 1. Mg \\ 2. CO_2 \\ 3. WK \\ \vdots. \end{array} $	$\frac{1. \text{ NaOH}}{2. \text{ Br}}$	1. excess CH <sub>3</sub> Li 2. WK
Br J.	→ <sup>0<sup>©</sup><sub>Na</sub>⊕</sup>	OsO <sub>4</sub>
		$\frac{1. \text{ NaH}}{2. \text{ Br}}$

4. The purpose of this problem is to test your "generalized" ability to write mechanisms. Predict reasonable products and provide a complete arrow-pushing mechanism (curved arrows, lone pairs and formal charge) to explain your product(s). If resonance structures are present, show at least one other resonance structure (make sure one of them is the "best" resonance structure) to demonstrate that you are aware of their presence. LDA is a strong electron pair donor, but is sterically bulky so it **only acts as a base**. (26 pts) a. (8 pts)

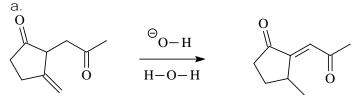
$$\underbrace{\overset{O}{\qquad}}_{O} \underbrace{\overset{1. 2 \text{ eqs. } CH_3^{\ominus} (MgBr)^{\oplus}}{2. H_3 O^{\oplus}/H_2 O} }_{O} \underbrace{C_4 H_{10} O_{+} C_2 H_6 O}$$



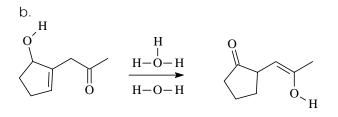




 Provide a complete arrow-pushing mechanism (curved arrows, lone pairs, formal charge, important resonance structures for the following transformations). Restrict your tautomeric changes to keto or enol portions of the molecules, not isolated carbon-carbon double bonds. If oxygen is part of an anionic or cationic resonance system, show that structure. (a = 10 pts, b = 15 pts, total 25 pts)



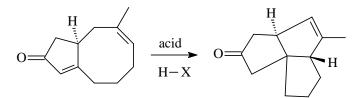
I count about 4 steps to do the job.



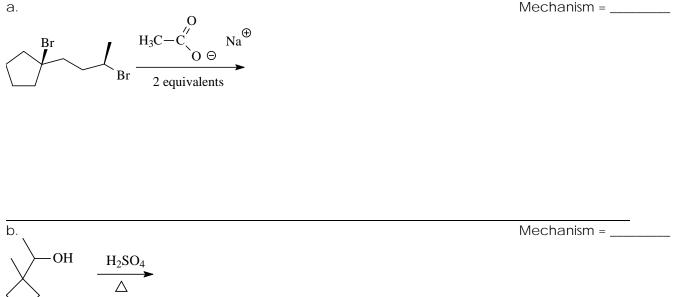
Be careful on this one. There is a deceptively easy way to write the mechanism...and it is wrong. You need to start at a keto or enol part of the molecule. I count about 6 steps to do the job.

6. Propose a reasonable synthesis for the following molecule. Your only source of <sup>14</sup>C is labeled methanol, \*CH<sub>3</sub>OH, and carbon dioxide, \*CO<sub>2</sub>. You may also use non-<sup>14</sup>C methanol, bromobenzene, ethene and propene, as well as any other routine reagents discussed in our course. Begin 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. (27 pts)

7. Propose a mechanism for the following reaction. Include all curved arrows, lone pairs and formal charge to show how the reaction proceeds. Also, draw out at least one additional resonance structure whenever reasonable resonance structures exist. Numbering your carbons may help. Remember what you've learned about where "keto/enol" problems need to begin in acid. I estimate it should take about 5 steps. (20 pts)



8. 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 = \_\_\_\_\_

9. 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 circle the appropriate letter indicating if the product(s) is(are) chiral (c), enantiomers (e), diastereomers (d), meso (m) or no chiral centers (n). 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. (28 pts)

Alkenes		
Reagent 1 K <sup>⊕</sup> MnO₄ <sup>⊖</sup>	(c) (e) (d) (m) (n) R/S	(c) (e) (d) (m) (n)
Reagent 2 Br2	(c) (e) (d) (m) (n) R/S	(c) (e) (d) (m) (n)

The future is purchased by the present. Samuel Johnson

Problem considered, but not used on this exam. Explain the difference in reactivity between the two ketones and provide a detailed arrow pushing mechanism.

