

California State Polytechnic University, Pomona

Chem 316
Final Exam
Winter, 2005
Beauchamp

Name: _____

Topic	Total Points Exam Points	Credit
1. Nomenclature (1)	25	
2. Explanation of Relative Aromatic Reactivities	20	
3. Reactions Page (10 x 3 = 30)	30	
4. Aromatic Mechanism and Explanation of Substituent Effects	25	
5. Mechanism (acidic conditions and base conditions)	30	
6. Combined Alkyne & Aromatic Mechanism and Explanation	20	
7. C-14 Synthesis (one nonaromatic & one with aromatic components included)	30	
8. Carbohydrate Game (reaction recognition/simplistic mechanisms)	20	
9. Free radical mechanism, predicting all distinct products, relative amounts and stereochemical features present	20	
Total	220	

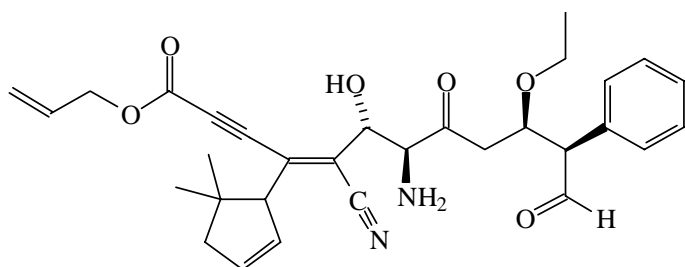
This is a long exam. It has been designed so that no one question will make or break you. The best strategy is to work steadily, starting with those problems you understand best. Make sure you show all of your work. Draw in any lone pairs of electrons, formal charge and curved arrows to show electron 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.

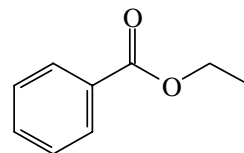
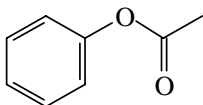
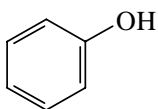
Dorothy Parker

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



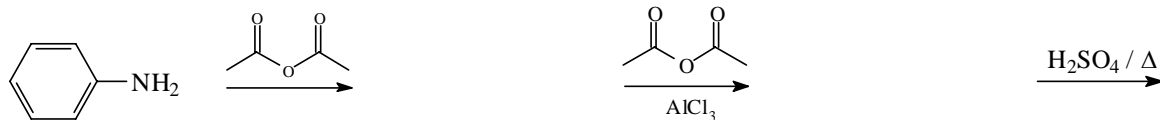
2. State whether each of the following aromatic substituents acts as an activating or deactivating group on the aromatic ring. Order the substituents in decreasing order of activating influence on the aromatic ring (1= most activating). Use structures to show your logic. Write out the reaction conditions and the expected sulfonation product in each case. (20 pts)



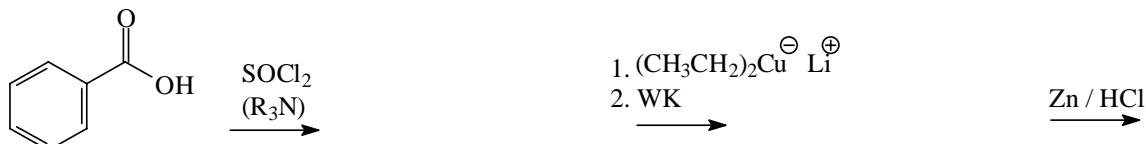
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3. Provide the expected product for each of the following transformations. Show regiochemistry and stereochemistry clearly, if relevant. Do NOT show mechanisms. WK = workup. (30 pts)

a.



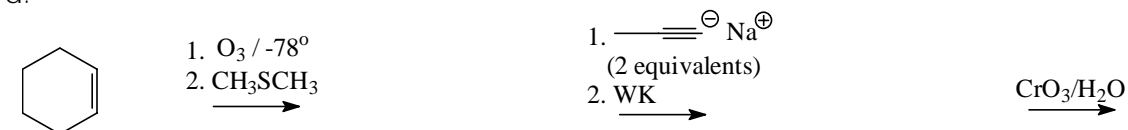
b.



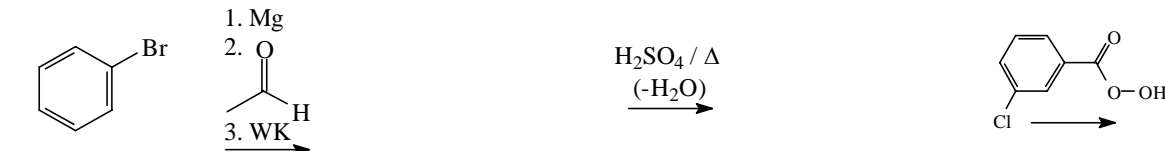
c.



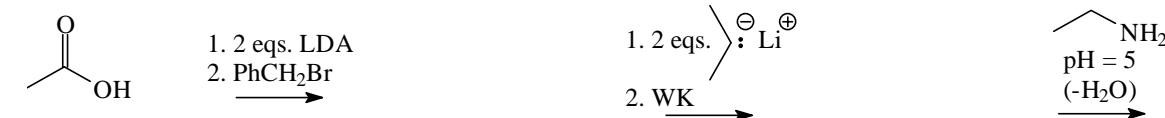
d.



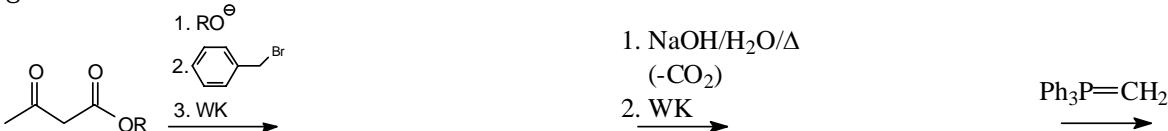
e.



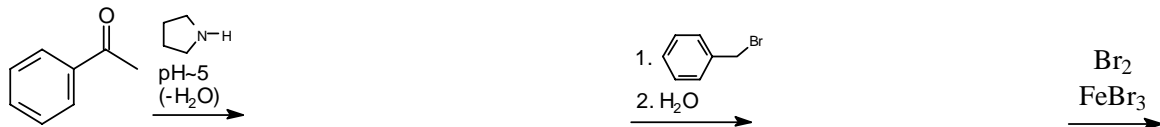
f.



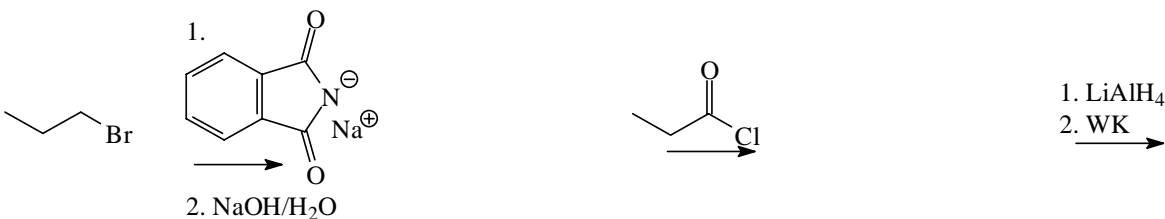
g.



h.



i.



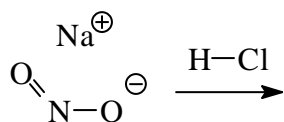
j.



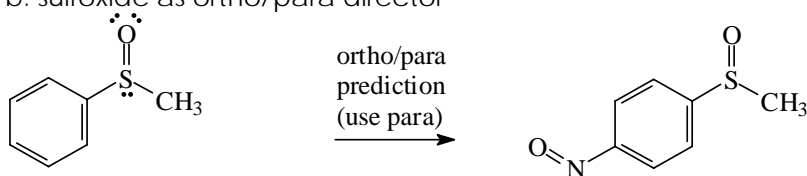
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4. Consider nitrosolation of phenyl methyl sulfoxide shown below. An argument can be made that the sulfoxide substituent is either an ortho/para director or a meta director. Show why an electrophile might prefer to attack ortho/para (show formation of the para product) and then show why an electrophile might prefer to attack meta. Explain your answer using appropriate structures of the intermediate, as well as providing a detailed mechanism for each possibility. Generate the nitrogen electrophile using a mixture of NaNO_2 and HCl . (25 pts)

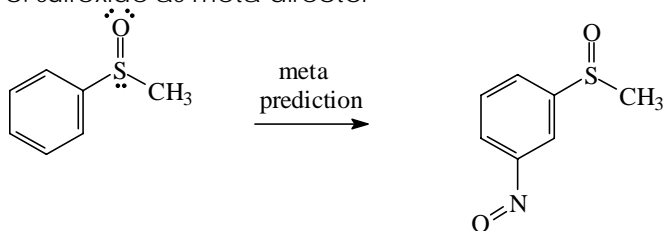
a. Generation of electrophile



b. sulfoxide as ortho/para director



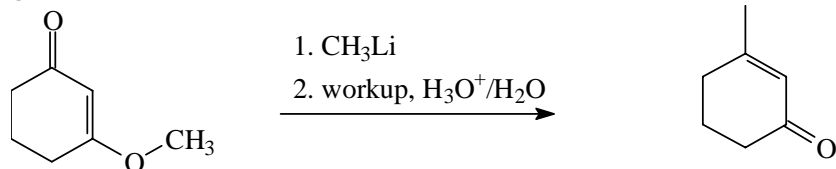
c. sulfoxide as meta director



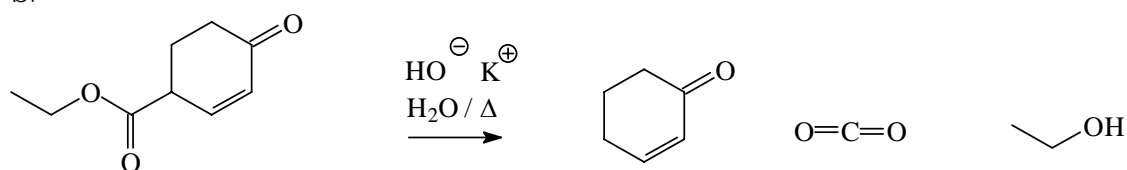
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5. Provide a complete arrow-pushing mechanism for the reaction below. Include curved arrows, lone pairs of electrons and formal charge. If resonance is present, draw at least one additional resonance structure to show you recognize this feature, and one of them should be the "best" resonance structure. (30 pts)

a.

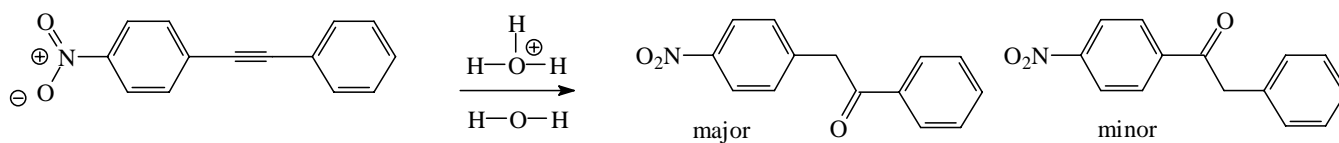


b.



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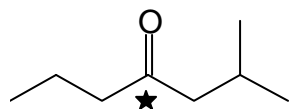
6. Explain the following observation. Include any structure(s) necessary for your explanation. Also include a correct arrow pushing mechanism for the major product. (20 pts)



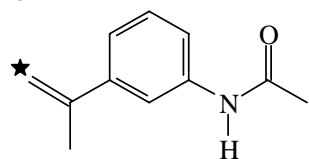
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7. Propose a synthesis for the following compound using methanol, ethane, propene, cyclohexene, benzene, sodium cyanide or carbon dioxide. Your only source of radioactive C-14 carbon is C-14 methyl bromide, *CH_3Br , carbon dioxide, *CO_2 and sodium 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)

a.



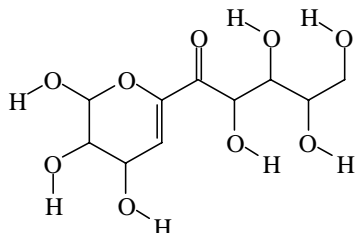
b.



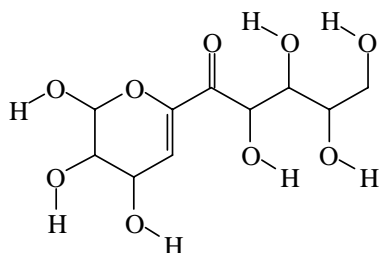
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8. From the given carbohydrate, use a simplistic nondetailed mechanism to show how each transformation could occur. Draw in any additional atoms needed to demonstrate your transformations (e.g. a hydrogen atom or a water molecule, etc.). Use **B:** if you need a base and **B-H⁺** if you need an acid. (20 pts)

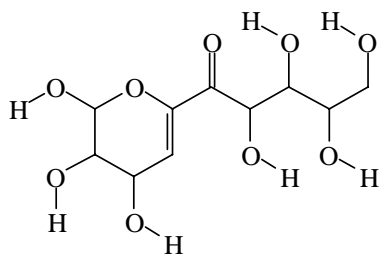
a. retroaldol to 3C and 7C structures



b. hemi-acetal formation to a favorable ring



c. a forward Michael reaction adding the "elements" of water



d. identify what two processes occurred and show how they happened



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9. a. How many different types of hydrogens are present in 2-methylbutane? How many products are formed when 2-methyl butane is brominated with $\text{Br}_2/h\nu$? If any chiral centers are present in the starting material or the products, draw them clearly with a 3D representation and specify the absolute configuration of each. If stereoisomers form, specify what type of isomerism is present (enantiomers, diastereomers, meso compounds, achiral, etc.). Indicate the approximate relative amounts of each product formed if the relative rates of reaction of a bromine atom with an sp^3 C-H bond are: primary = 1, secondary = 80 and tertiary = 1600. (10 pts)

b. Provide a complete arrow pushing mechanism to explain formation of the major product from the above reaction (show proper curved arrow conventions, lone pairs as two dots and single electrons as one dot). Clearly label each distinct part of the reaction mechanism. Calculate an overall ΔH for each step of your mechanism using the given bond energies. (10 pts)

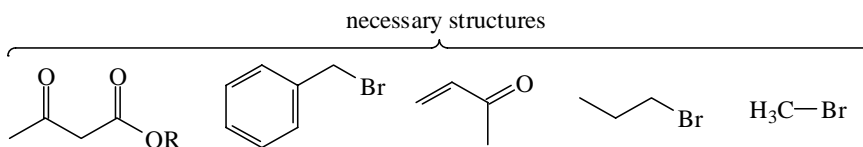
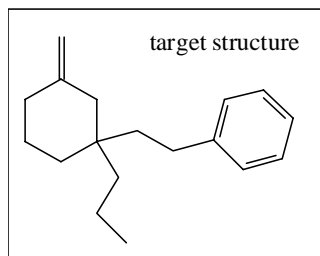
	ΔH (kcal/mol)
Br—Br	46
H—Br	87
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$\text{Me}^{\circ}\text{C—H}$	105
1°C—H	98
2°C—H	95
3°C—H	92
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$\text{Me}^{\circ}\text{C—Br}$	70
1°C—Br	68
2°C—Br	68
3°C—Br	65

The immediate is often the enemy of the ultimate.

Indira Gandhi

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Problems considered, but not given on this exam. Propose a synthesis for the following molecule using the given structures (you will have to use them all). You can use any other routine organic reagents that we have studied, as well. Work your way backwards to the starting material using the Grignard reaction as the last step. (20 pts)



Necessary reactions in order of reaction:

1. dianion reaction (use LDA as your base)
2. Robinson's annelation (use RO^- as your base) = two reactions: a. Michael rxn b. aldol rxn
3. hydrolysis and decarboxylation (use NaOH)
4. cuprate conjugate addition (make your own cuprate reagent)
5. Wittig reaction (make your own Wittig salt)

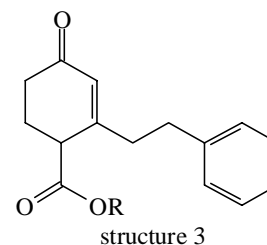


structure 1

structure 2



structure 2



structure 3

structure 4

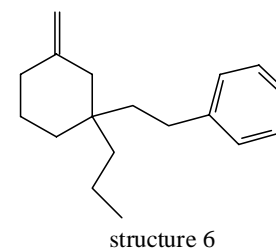


structure 4

structure 5



structure 5



Extra problems

