California State Polytechnic University, Pomona

Chem 316
Final
Spring, 2004
Beauchamp

Name: _____

Topic	Total Points Exam Points	Credit
1. Nomenclature (1)	25	
2. Tautomers (acidic or base conditions)	20	
3. Reactions Page (10 x 3 = 30)	30	
4. Aromatic Mechanism and Explanation of Substituent Effects	20	
5. Arrow Pushing Explanation	12	
6. Explanation of Relative Reactivities of carbonyls	20	
7. Combined Arrow-pushing Mechanism, several functional groups	25	
8. Questions related to pharmaceutical topic	20	
9. C-14 Synthesis (Aromatic Components Included)	25	
10. Carbohydrate Game (reaction recognition/simplistic mechanisms)	28	
11. Free Radical Mechanism, Product Ratio, Stereochemistry	25	
Total	240	

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 keys to heaven also open the gates of hell. Buddhist saying

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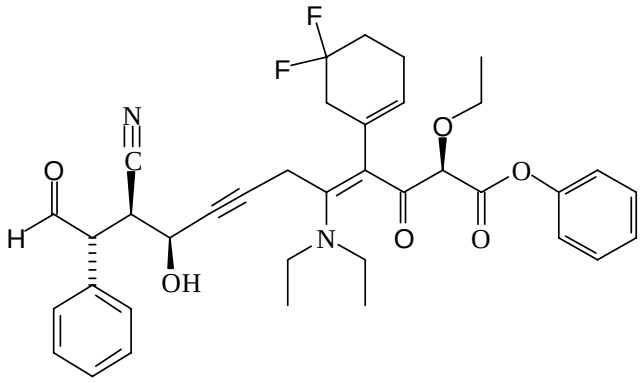
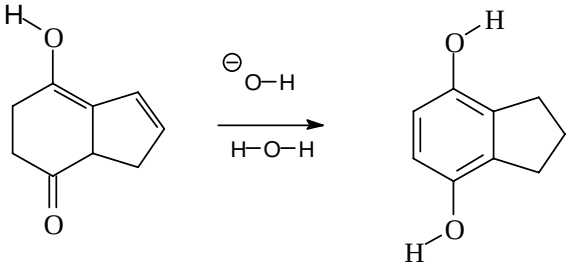
1. Provide an acceptable name for the following structure. (25 pts)



2. Provide a complete arrow-pushing mechanism for the reaction below. Include curved arrows, lone pairs of electrons, formal charge and important resonance structures. Restrict your mechanism to keto or enol forms, not isolated carbon/carbon bonds. (20 pts)



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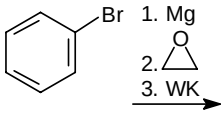
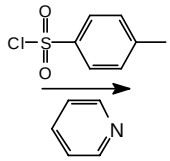
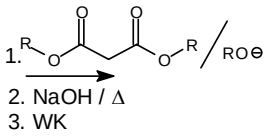
3. Provide the expected product for each of the following transformations. Show regiochemistry and stereochemistry clearly, if relevant. Do NOT show mechanisms. WK = workup. (30 pts)

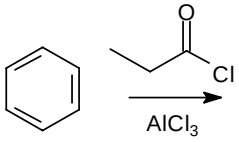
a.

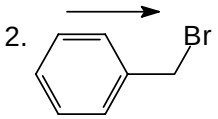


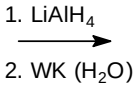




b.







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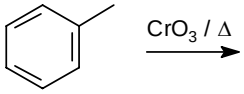

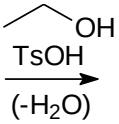

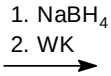

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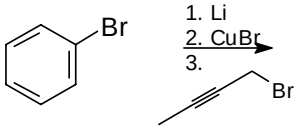

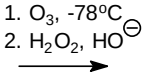

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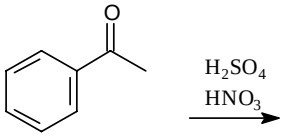
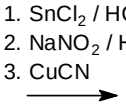
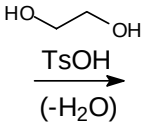
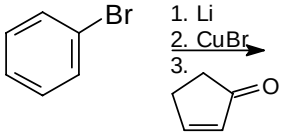
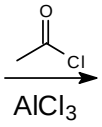


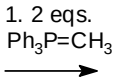




f.







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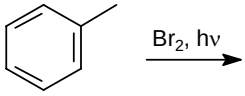

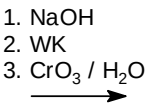

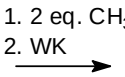

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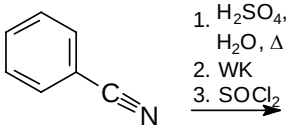
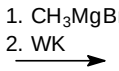
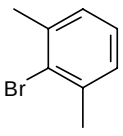
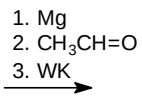
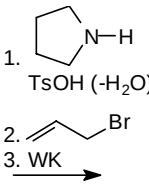




i.







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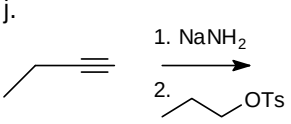
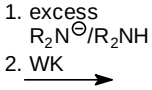
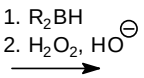
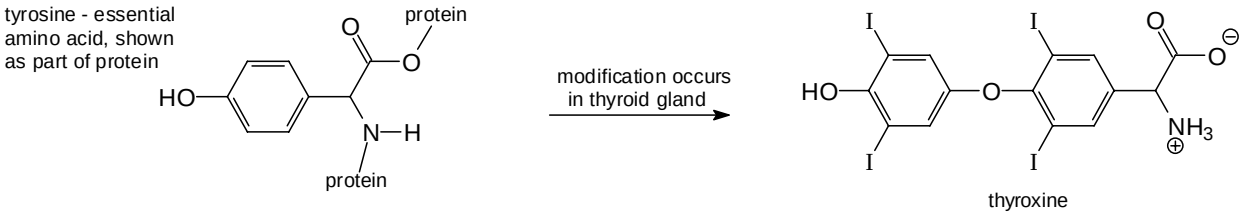


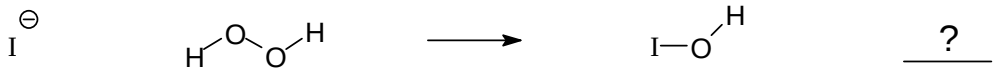




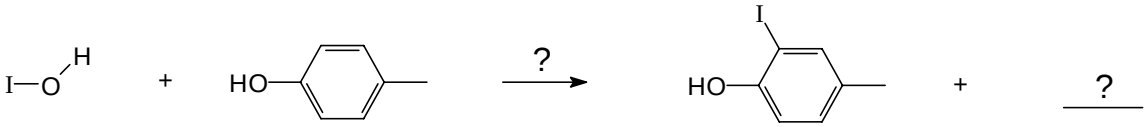
4. Thyroxine is an important hormone in the body used to help control our rate of metabolism. It is made from our amino acid tyrosine in a series of steps. The aromatic rings have to be iodinated before tyrosine becomes thyroxine. This requires an electrophilic form of iodine that must be made by the body since we only consume nucleophilic iodide in our diet. The relatively rare iodide is sequestered in our thyroid gland. It is very likely that a form of peroxide is used to do this.



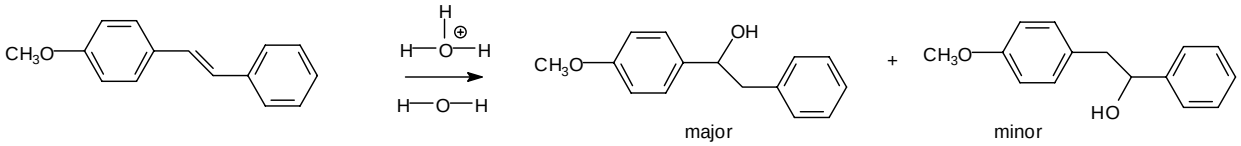
a. Using simple hydrogen peroxide (the form usually written in a biochem textbook) and iodide, show how electrophilic iodide might be made. Explain how this reaction makes the iodine electrophilic. (5 pts)



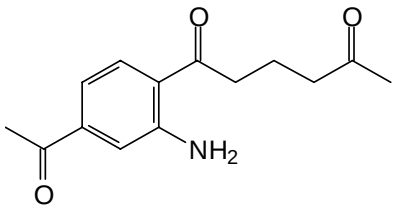
b. Show why it make sense that the iodine atoms end up at the positions that they do in throxine? Use p-methylphenol (as a simple approximation of tyrosine going to thyroxine). Use the electrohphile from part a to show the incorporation of a single iodine atom. Explain fully why the regiochemistry observed occurs the way it does. (15 pts)



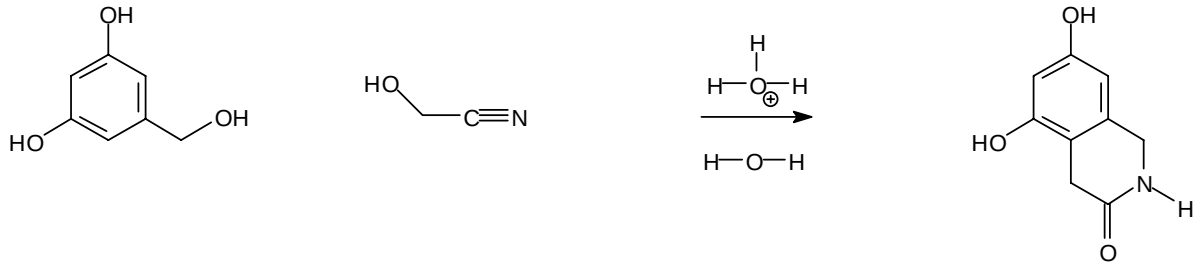
5. Explain the following observation. Include any structure(s) necessary for your explanation. Also include correct arrow pushing conventions, where appropriate. (12 pts)



6. Order the carbonyls in decreasing order of reactivity towards nucleophiles (1= most reactive). Use structures to show your reasoning. (20 pts)



7. Propose a step-by-step mechanism using curved arrows to show the flow of electrons. Use "Ar" as a short hand for the aromatic ring when it is not an essential part of your mechanism. (25 pts)



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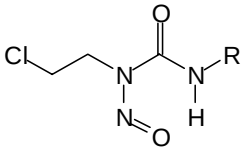
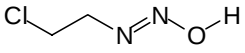
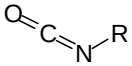
8. A class of compounds (2-chloroethyl)nitrosoureas are used as anti-cancer drugs. Their mechanism of drug action cross links DNA (connects distant parts of DNA together). The following steps are provided (with simplified structures) showing how this likely occurs. Provide the mechanistic detail to show how each step occurs (curved arrows, lone pairs and formal charge, where needed). (20 pts)

a. decomposition of (2-chloroethyl)nitrosourea





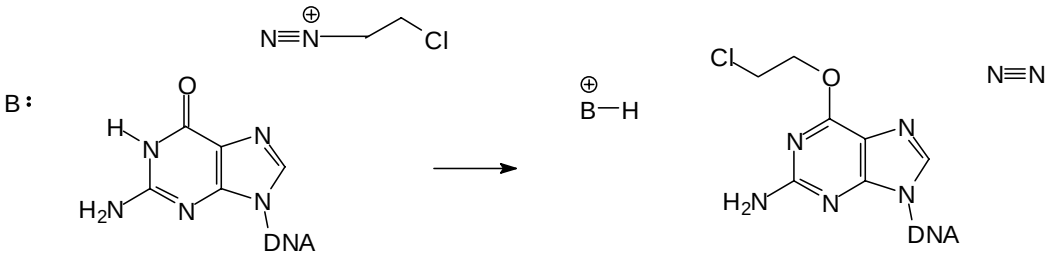
further reaction (see b) leads to a (2-chlorethyl)diazonium comound



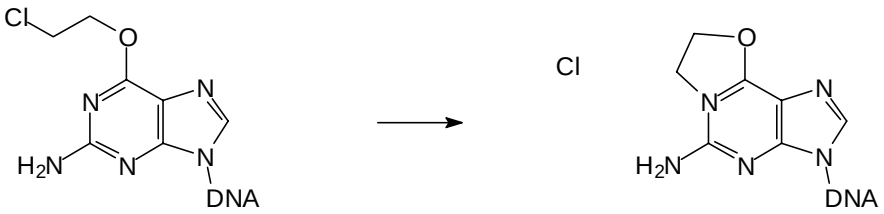
alkylisocyanate - can form carbamates with "O" nucleophiles, but if changed to an OR or R the starting structure still has anti-cancer activity, implying that the structure to the left gives rise to the anti-cancer activity

b. formation of anti-cancer diazonium compounds

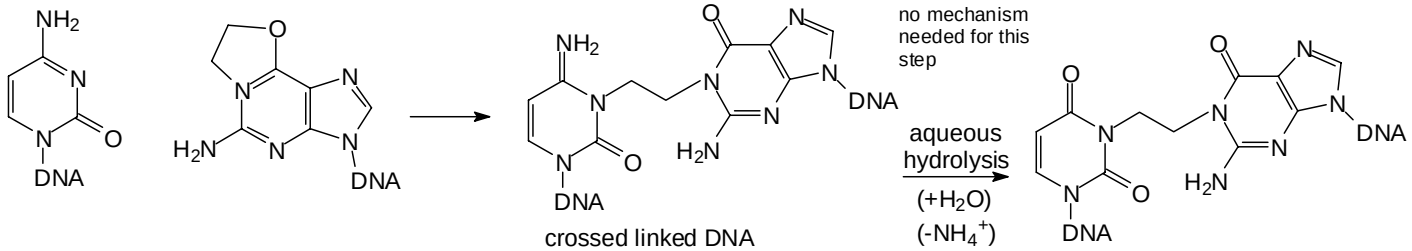
c. alkylation of first DNA base



d. intramolecular reaction of DNA base



e. reaction with second DNA base to produce cross linking of DNA



crossed linked DNA

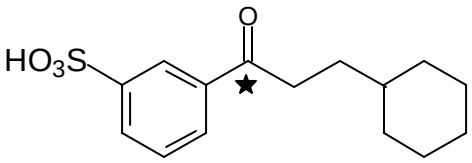
no mechanism needed for this step

aqueous hydrolysis

$(+H_2O)$

$(-NH_4^+)$

9. Propose a synthesis for the following compound using methanol, ethanol, propene, cyclohexane, benzene, sodium cyanide or carbon dioxide. Your only source of radioactive C-14 carbon is C-14 methyl bromide, CH_3Br, sodium cyanide, Na*CN and carbon dioxide, $*CO_2$. 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)



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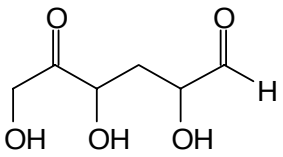
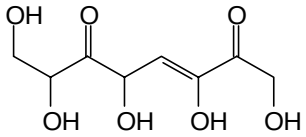
10. From the given carbohydrate, use a simplistic nondetailed mechanism to show how each transformation could occur. Draw in any additional atoms needed to demonstrate your transformations (e.g. a hydrogen atom or a water molecule, etc.). Use **B:** if you need a base and **B-H$^{\oplus}$** if you need an acid. (28 pts)

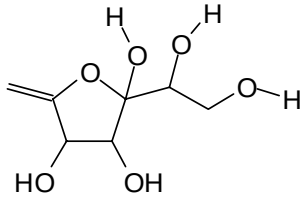
a. aldol to form a 6 atom ring, followed by a reverse Michael



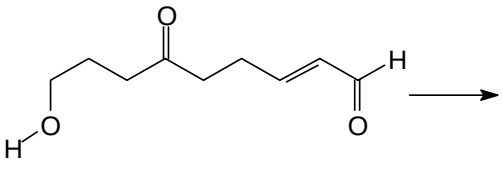
b. Michael addition (hydration) to a conjugated carbonyl, retro-aldol to 5C and 3C structures

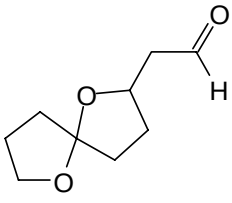


c. retro-hemi-ketal formation, keto/enol tautomerization to a diketone, forward hemi-ketal forming 6 atom ring.

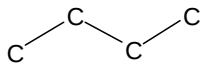


d. identify what process happened and show how they happened.

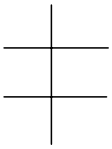


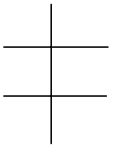


11. a. Chlorination of (2R)-2-phenylbutane produces six different substitution products. Show each of these possible products (show in 3-D and identify absolute configuration of chiral centers where stereochemistry is important). Indicate the approximate relative amounts formed (assume relative rates are: primary = 1, secondary = 4, tertiary = 10 when R = phenyl). If stereoisomers are present indicate if they are enantiomers, diastereomers, meso, etc. Use Fischer projections. (15 pts)



3D structure of
(2R)-2-phenylbutane

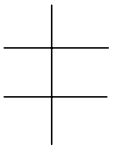


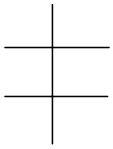


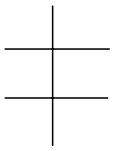
Fischer projection

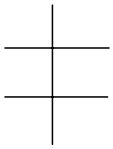
Cl—Cl

hν

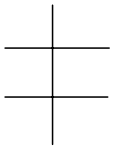








six possible
chlorination products



b. Propose a complete mechanism to explain formation of a **major product** (show proper curved arrow conventions and electrons as dots). Clearly label each distinct part of the mechanism (10 pts)

1.

2.

3.

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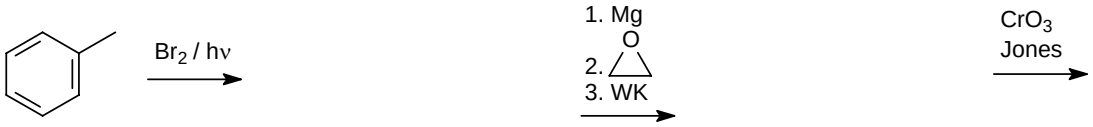
Preview of Exam Questions – Certain key phrases may be left out of the following preview.

1. Provide an acceptable name for the following structure. (20 pts/15 pts)

2. 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.



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/22 pts)

4. Consider…("an aromatic reaction")…shown below. …etc… Explain your answer using appropriate structures of the intermediate, as well as providing a detailed mechanism for each possibility. Generate the … "electrophile" …etc. (25 pts/18 pt)

5. Explain the following observation. Include any structure(s) necessary for your explanation. Also include correct arrow pushing conventions, where appropriate. (10 pts/7 pts)

6. State whether … is an activating or deactivating group. Order …"etc"… in decreasing order …(1= most …). Use structures to show your logic. Write out the expected … product in each case (20 pts/15 pts)

7. "Miscellaneous information provided…". Propose a step-by-step mechanism using curved arrows to show the flow of electrons. (Hint: the carbonyl group is protonated first. What have you formed when this happens?) (20 pts/15 pts)

8. Develop a molecular orbital argument to explain how the Diels-Alder reaction works. Parts a, b, c, d and e. (25 pts/18 pts)

9. Propose a synthesis for the following compound using methanol, ethanol, propene, cyclohexene, benzene, sodium cyanide or carbon dioxide. Your only source of radioactive C-14 carbon is C-14 methyl bromide, $*CH_3Br$. 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/15 pts)

10. 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**$^{\oplus}$ if you need an acid. Parts a, b, c, d, e and f. (30 pts/22 pts)