## Califomia State Polytechnic University, Pomona

## Chem 316

Final Exam
Winter, 2007
Beauchamp
Name: $\qquad$

| Topic | Total Points Exam Points | Credit |
| :---: | :---: | :---: |
| 1. Nomenclature (1) | 25 |  |
| 2. Explanation of Relative Reactivities of Aromatic Compounds orCarbonyl Compounds | 20 |  |
| 3. Reactions Page ( $10 \times 3=30)$ | 30 |  |
| 4. Tautomers (acidic conditions and base conditions) | 30 |  |
| 5. Aromatic Mechanism and Explanation of Substituent Effects | 30 |  |
| 6. C-14 Synthesis | 30 |  |
| 7. Bio-organic Game (reaction recognition/simplistic mechanisms) | 52 |  |
| 8. Carbonyl Chemistry - synthesis a nd mec ha nisms | 28 |  |
| Total | 245 |  |

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 a rrowsto 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.

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

## Califomia State Polytechnic University, Pomona

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

2. State whethereach of the following a romatic substituents acts as an activating ordeactivating group on the aromatic ring. Orderthe substituents in decreasing order of activating influence on the aromatic ring ( $1=$ most activating). Use structures and a brief explanation to rationalize your order. Write out the reaction conditions for bromination and the expected product in each case. ( 20 pts )




## Califomia State Polytec hnic University, Pomona

3. Provide the expected product foreach of the following transformations. Show regiochemistry and stereoc hemistry clearly, if relevant. Do NOTshow mechanisms. WK = workup. (30 pts) a.

b.

$\xrightarrow{\substack{\text { a. } \mathrm{RO}^{\ominus} / \mathrm{ROH} \\ \text { b. } \mathrm{CH}_{3} \mathrm{I}}} \quad \xrightarrow{\text { 1. } \mathrm{NaOH}} \begin{aligned} & \text { 2. } \mathrm{H}_{3} \mathrm{O}^{+} / \Delta\end{aligned}$
4. 2 eqs. $\mathrm{CH}_{3} \mathrm{MgBr}$
5. WK

a. Li
b. $\mathrm{H}_{2} \mathrm{C}=\mathrm{O}$
c. WK
$\xrightarrow{\substack{\mathrm{CrO}_{3} / \mathrm{H}_{2} \mathrm{O} \\ \text { Jones }}}$

a. KOH
b. WK
6. LDA, $-78^{\circ} \mathrm{C}$
$\xrightarrow{\text { 2. }}$
$\xrightarrow{\text { a. } \xrightarrow{\mathrm{H}_{3} \mathrm{O}^{+} / \mathrm{H}_{2} \mathrm{O}} \text { ( }}$
7. TsCl / pyridine

2a. $\mathrm{LiAlH}_{4}$
b. WK
$\xrightarrow{\begin{array}{l}\text { 1. } \mathrm{PCC} \\ \text { 2. } \mathrm{Ph}_{3} \mathrm{P}=\mathrm{CH}_{2}\end{array}}$

1. $\mathrm{SOCl}_{2}$
2. $\left(\mathrm{CH}_{3}\right)_{2} \mathrm{NH}$
a. DIBAH
( $\mathrm{R}_{2} \mathrm{AlH}$ )
b. WK
a. $\mathrm{NaNO}_{2} / \mathrm{HCl}$
$\xrightarrow{\text { b. } \mathrm{CuCN}}$
$\mathrm{NH}_{2} \mathrm{NH}_{2}$
$\xrightarrow{\mathrm{RO}^{\ominus} / \Delta}$


## Califomia State Polytechnic University, Pomona

4. Provide a complete arrow-pushing mechanism for each reaction below. Include curved arrows, lone pairs of electrons and fomal 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.




## Califomia State Polytechnic University, Pomona

5. Starting from benzene, propose a synthesis for each of the following molecules. Provide mechanisms that show how any necessary electrophiles are generated. Provide a mechanism forthe second reaction step that expla ins the observed regioselectivity (ortho, para or meta) in each of your proposed syntheses. ( 25 pts )
a. Synthetic targets - Propose a synthetic sequence that leads to each molecule. No mechanisms are required here. (4 pts)
i.


ii.


b. Provide mechanisms forgenerating any electrophiles used in the above synthetic sequences. (6 pts)
i.
ii.

## Califomia State Polytec hnic University, Pomona

c. Provide a mechanistic explanation that explains the observed regioselectivity in each reaction in part a. (20 pts)
i.
ii.

## Califomia State Polytechnic University, Pomona

6. Propose a synthesis for the following compound using methane, ethane, propane, cyclohexane, benzene, sodium cyanide and/orcarbon dioxide. Your only sources of radioactive ${ }^{14} \mathrm{C}$ carbon are methyl bromide, ${ }^{+} \mathrm{CH}_{3} \mathrm{Br}$, carbon dioxide, * $\mathrm{CO}_{2}$ a nd sodium cyanide, $\mathrm{Na} \mathrm{C}^{\mathrm{CN}}$. You may also use any typic al 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 foreach backwards step until you reach allowable starting molecules. Do not show mechanisms. (30 pts)


## Califomia State Polytechnic University, Pomona

7. From the given bio-orga nic structure, use our simplistic mec ha nisms to show how each tra nsformation could occur. If any structures are missing, use the descriptive term to fill in the necessary structures and details. Draw in any additional atoms or structures needed to demonstrate the transformations (e.g. a hydrogen atom or a water molecule, any co-factors, etc.). Use $\mathbf{B}$ : if you need a base and $\mathbf{B}-\mathbf{H}^{\oplus}$ if you need an acid. Acceptable representations of possible co-factors are provided at the bottom of the last page. (52 pts) a.


b.


$\qquad$





## Califomia State Polytechnic University, Pomona

C.

.

retro-aldol

d.
d.


e.


## Califomia State Polytechnic University, Pomona

8. a. Provide the necessary starting materials and a complete a row pushing mechanism to explain formation of the indic ated product (show propercurved a rrow conventions, lone pairs as two dots and single electrons as one dot). You only need to show the most important resonance structure and ( $\leftarrow \rightarrow$ Res.) whenever resonance is present. The necessary starting structures will be supplied for 3 points (10 pts)

b. Provide a detailed mechanism for the next step of the synthesis. You only need to show the most important resonance structure and ( $\leftarrow \rightarrow$ Res.) whenever resonance is present. ( 8 pts )




## Califomia State Polytechnic University, Pomona

c. Provide a detailed mechanism for the next step of the synthesis. You only need to show the most important resonance structure and ( $\leftrightarrow \rightarrow$ Res.) whenever resonance is present. Indicate what products $x$ and y are. (10 pts)


product x
product y

Simplified co-factors for the bio-organic game problems, if needed.

$\mathrm{NAD}^{+}$
equivalent

NADH
equivalent

TPP ylid

ATP

vitamin B-6
( $1^{0}$ amine version)

vitamin B-6 (aldehyde version)

The pessimist complains about the wind, the optimist expects it to change and the realist adjusts the sails.

Califomia State Polytechnic University, Pomona







