Chem 51C Final Exam  
183 points; 2 hours  
June 10, 2015 

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**Academic Honesty Policy.** Academic honesty is strictly enforced on quizzes, exams, and other aspects of this course. Academic dishonesty will result in a failing grade in the class and a letter in the student's file. Activities constituting academic dishonesty include:

**Cheating**  
- Copying from others during an examination.  
- Communicating exam answers with other students during an examination.  
- Offering another person's work as one's own.  
- Taking an examination for another student or having someone take an examination for oneself.  
- Tampering with an examination after it has been corrected, then returning it for more credit.  
- Using unauthorized materials, prepared answers, written notes, or concealed information during an examination.

**Dishonest Conduct**  
- Stealing or attempting to steal an examination or answer key from the instructor.  
- Allowing another student to copy off of one's own work during a test.

**Collusion**  
- Any student who knowingly or intentionally helps another student perform any of the above acts is subject to discipline for academic dishonesty.

I understand and will abide by this academic honesty policy: __________________________ (signature)  

Seat: ________
1. Write the missing reactants, reagents, and products in the boxes. If NO REACTION OCCURS, write N.R. (24 points, 3 points each)
2. Write the missing reactants, reagents, and products in the boxes. If NO REACTION OCCURS, write N.R. (24 points, 3 points each)
3. Write the missing reactants, reagents, and products in the boxes. If NO REACTION OCCURS, write N.R. (24 points, 3 points each)
4. The aldol reaction, Michael reaction, Robinson annulation, and Claisen reaction provide powerful tools to build complex molecules from smaller components. These reactions give rise to products such as β-hydroxycarbonyl compounds, α,β-unsaturated carbonyl compounds, 1,5-dicarbonyl compounds, cyclohexenones, and β-ketoesters, which can be further elaborated through reactions such as the Wittig reaction, the addition of organometallic reagents, or reduction. Using these and other reactions, design good syntheses of the following compounds starting with compounds containing EIGHT (8) carbon atoms or fewer as the only organic starting materials. You may use any other inorganic reagents you choose and organic reagents that don't get incorporated into the final product, such as TBDMSCl, Ph₃P, LDA, PCC, DCC, p-TsOH, TsCl, etc. You may also use Wittig reagents, such as Ph₃P=CH₂, and organometallic reagents, provided that they don't add more than EIGHT (8) carbon atoms to the product. **Hint:** Each of these compounds can be constructed in two steps.

Select three of the following four problems. (6 points each, 18 points total). Cross out the problem that you do not wish to answer, or only the first three problems will be graded.

a. 

b. 

c. 

d.
5. Salicin is an analgesic and anti-inflammatory, related to aspirin, that occurs in the bark of willow trees. Treatment of salicin with strong acid in methanol yields salicyl alcohol and a mixture of methyl β-D-glucopyranoside and methyl α-D-glucopyranoside.

Write a curved-arrow mechanism for this reaction, illustrating the formation of salicyl alcohol, methyl β-D-glucopyranoside, and methyl α-D-glucopyranoside. Make sure to show each step of the reaction and all reactants, intermediates, products, charges, and important lone pairs of electrons. (16 pts)
6. In the Baylis-Hillman reaction, an α,β-unsaturated carbonyl compound and an aldehyde combine in the presence of a tertiary amine catalyst. The reaction may be thought to proceed by a set of four steps: (1) conjugate addition of the tertiary amine to the α,β-unsaturated carbonyl compound to generate a zwitterionic enolate; (2) aldol reaction of the zwitterionic enolate with the aldehyde to give an aldolate; (3) proton transfer(s) to generate another enolate; and (4) elimination to generate the Baylis-Hillman product.

Methyl acrylate and acetaldehyde react to form the Baylis-Hillman product shown below.

![Chemical Structure]

Write the structures of the intermediates of the Baylis-Hillman reaction in each of the boxes. If you wish to receive partial credit for incorrect answers based on sound mechanistic principles, you may draw curved arrows to help us understand your thinking. (15 points)

Step 1

![Chemical Structure]

Step 2

![Chemical Structure]

Step 3

![Chemical Structure]

Step 4

![Chemical Structure]
7. In the Favorskii rearrangement, an α-halo ketone reacts with an alkoxide base to form an ester. The reaction may be thought of as proceeding by a set of five steps: (1) formation of an enolate (the less substituted enolate); (2) intramolecular S_N2 reaction (or a stepwise process) to form a cyclopropanone; (3) addition of alkoxide base to the carbonyl group of the cyclopropanone to form a tetrahedral intermediate; (4) ring opening of the tetrahedral intermediate to form a carbanion intermediate (called a homo enolate); and (5) protonation of the carbanion intermediate to generate the Favorskii rearrangement product.

2-Chlorocyclohexanone reacts with sodium methoxide to form methyl cyclopentanecarboxylate as shown below.

Write the structures of the intermediates of the Favorskii rearrangement in each of the boxes. If you wish to receive partial credit for incorrect answers based on sound mechanistic principles, you may draw curved arrows to help us understand your thinking. (20 points)
8. Shown below are the 20 amino acids common in proteins. (18 points, 6 points each).

- Alanine (Ala, A)
- Valine (Val, V)
- Leucine (Leu, L)
- Isoleucine (Ile, I)
- Phenylalanine (Phe, F)
- Tyrosine (Tyr, Y)
- Proline (Pro, P)
- Glycine (Gly, G)
- Serine (Ser, S)
- Threonine (Thr, T)
- Cysteine (Cys, C)
- Methionine (Met, M)
- Aspartic Acid (Asp, D)
- Asparagine (Asn, N)
- Glutamic Acid (Glu, E)
- Glutamine (Gln, Q)
- Lysine (Lys, K)
- Arginine (Arg, R)
- Histidine (His, H)
- Tryptophan (Trp, W)

a. Draw the structure of the pentapeptide LVFFA (Leu-Val-Phe-Phe-Ala), an important piece of the β-amyloid polypeptide (Aβ), which forms plaques in Alzheimer's disease.

b. Write out all the steps in the synthesis of the pentapeptide LVFFA (Leu-Val-Phe-Phe-Ala). Use a benzyl ester as the C-terminal protecting group and tert-butoxycarbonyl (Boc) as the N-terminal protecting groups. Use dicyclohexylcarbodiimide (DCC) as the coupling agent to form the amide bonds. You may use any protected amino acids that you require.

c. Treatment of the pentapeptide LVFFA (Leu-Val-Phe-Phe-Ala) with dicyclohexylcarbodiimide (DCC) gives a product with the molecular formula C_{32}H_{43}N_{5}O_{6}. (Note that the LVFFA pentapeptide has a molecular formula C_{32}H_{43}N_{5}O_{6}. ) Write the structure of the product.
9. Shown below are molecular models of aldohexoses in their pyranose forms. Under each molecular model write the name of the corresponding structure. If, for example, the structure is the enantiomer of \( \alpha \)-D-glucose, you would write: \( \alpha \)-L-glucose. Fisher projections of the D-aldohexoses in the open (aldehyde) form are provided for reference. (24 points)

Name: \( \text{\textbeta-} \text{D-\textg{l}{ucose}} \)
Name: \( \text{\textalpha-} \text{D-\textm{n}{annose}} \)
Name: \( \text{\textbeta-} \text{D-\textg{l}{ucose}} \)
Name: \( \text{\textbeta-} \text{L-\textg{l}{ucose}} \)
Name: \( \text{\textalpha-} \text{D-\textg{l}{ucose}} \)
Name: \( \text{\textbeta-} \text{D-\textg{l}{ucose}} \)