Chem 51C Final Exam  
177 points; 2 hours  
June 12, 2012

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<th>Problem</th>
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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. (27 points, 3 points each)

- From 4/5 lecture
  \[
  \text{NaBH}_4 \quad \text{EtOH} \quad \text{mixture of diastereomers}
  \]

- From 4/10 lecture
  \[
  \text{1. CH}_3\text{Li (2 equiv)} \quad \text{2. H}_2\text{O}^+ \quad \text{CH}_3\text{OH}
  \]

- From 4/12 lecture
  \[
  \text{1. DIBAL-H} \quad \text{2. H}_2\text{O (aq, H}_2\text{O)}
  \]

- From 4/17 lecture
  \[
  \text{a hydrocarbon}
  \]

- From 4/19 lecture
  \[
  \text{+ benzene reflux} \quad \text{(Dean-Stark trap)} \quad (+ \text{H}_2\text{O})
  \]

- From 4/24 lecture
  \[
  \text{+ cat. pTsOH} \quad (+ \text{H}_2\text{O})
  \]

- From 4/26 lecture
  \[
  \text{+ EIOH} \quad (+ \text{HCl})
  \]

- From 5/1 lecture
  \[
  \text{+ CH}_3\text{OH}
  \]

- From 5/3 lecture
  \[
  \text{cat. DCl} \quad \text{D}_2\text{O (solvent)}
  \]
2. Write the missing reactants, reagents, and products in the boxes. If NO REACTION OCCURS, write N.R. (27 points, 3 points each)
3. Write the missing reactants, reagents, and products in the boxes. If NO REACTION OCCURS, write N.R. (27 points, 3 points each)
4. Fructose exists in solution as an equilibrium mixture of furanose and pyranose forms comprising 31% of the β-furanose, 9% of the α-furanose, 57% of the β-pyranose, and 3% of the α-pyranose, along with 0.25% of the open (ketone) form. Using the template below, write a curved-arrow mechanism for the isomerization of the β-furanose form to the β-pyranose form. Make sure to show each step of the reaction and all reactants, intermediates, products, charges, and important lone pairs of electrons. (24 pts)
5. Cooking transforms food into tasty and good-smelling chemical compounds through chemical reactions similar to those that we've learned in class. The reactions involve carbonyl chemistry and may be thought of as being catalyzed by the \( \text{H}_2\text{O}^+ \) that is naturally present in water. (24 points)

a. Upon heating at high temperatures, sugars undergo caramelization to produce flavorful, good-smelling compounds, and colored compounds. Some of the caramelization reactions involve dehydration (loss of water) to give unsaturated compounds. One such product is hydroxymethylfurfural \([5-(\text{hydroxymethyl})-2\text{-furaldehyde}]\), which can form from glucose or fructose. Hydroxymethylfurfural may be thought of as forming from the furanose form of fructose, by way of a series of intermediates: (1) an enol intermediate, (2) an aldehyde intermediate, and (3) an \( \alpha,\beta \)-unsaturated aldehyde intermediate. Write the structures of the enol and \( \alpha,\beta \)-unsaturated aldehyde intermediates in the boxes.

b. Other caramelization reactions of sugars involve the breakdown of the sugars to form smaller volatile compounds and smaller sugars. D-Glucose can undergo retro-aldol (reverse aldol) reaction to form an aldotetrose (1) and a two-carbon enediol intermediate (2) that tautomerizes to the corresponding two-carbon aldehyde, glycolaldehyde (3). Write the structures of the aldotetrose, the enediol intermediate, and glycolaldehyde in the boxes.

c. Sugars and proteins taste even better when combined through cooking. Upon cooking, sugars combine with amino acids, peptides, and proteins through Maillard reactions, which occur in the browning of food during cooking, to give complex flavorful molecules. The Amadori rearrangement is one of the early-stage Maillard reactions and involves the combination of sugars and aldehydes to form ketoamine products, which can undergo further dehydration to give colored unsaturated compounds that make the food appear brown. The Amadori reaction may be thought of as occurring through the reaction of a lysine residue in a protein with D-glucose to give a ketoamine and imine, ending by way of a series of intermediates: (1) a hemiaminal intermediate, (2) an imine intermediate, and (3) an enamine intermediate. Write the structures of the hemiaminal, imine, and enamine intermediates in the boxes.
6. 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 SEVEN (7) 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 TBDMS, 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 SEVEN (7) carbon atoms to the product. **Hint:** Each of these compounds can be constructed in two steps.

Select four of the following six problems. (6 points each, 24 points total). Cross out the two problems that you do not wish to answer, or only the first four problems will be graded.
7. 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 α-D-glucose, you would write: α-L-glucose. Fisher projections of the D-aldhexoses are provided for reference. (24 points)

- Name: D-β-D-glucose
- Name: α-D-galactose
- Name: α-D-altrose
- Name: β-D-glucose
- Name: β-D-mannose
- Name: D-talose
- Name: D-gulose
- Name: D-idose
- Name: D-galactose

PLEASE REVIEW THE ACADEMIC HONESTY STATEMENT ON PAGE 1 AND SIGN IT IF YOU ARE ABLE