Exam 3  
Chemistry 52  
August 15, 2011  
7-9 pm

Do not open or begin this exam until instructed. This exam consists of 8 pages plus the cover page. Before starting the exam, check to make sure that you have all of the pages. The exam has a total of 130 points and includes 13 questions. Only legible answers written on the exam will be considered for grading. All pertinent information needed for the exam is given. Notes, textbooks, and electronic communication devices are not permitted. This exam is administered under the Dartmouth College Honor Principle.

Use your time wisely.

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<tr>
<th>Page Number</th>
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1. (5 points) Provide the structure of LDA. What does LDA abbreviate? (Provide the full name.)

2. (3 points) Provide an IUPAC accepted name for the following compound.

3. (12 points) Arrange the following compounds in order of increasing acidity. Estimate the pKa values of each acid. (Put letters in boxes and the corresponding pKa’s on the line under the box.)

4. (5 points) 2-Amino-1-phenylpropan-1-ol has long been an ingredient in many cold remedies and appetite suppressants. In late 2000, the FDA asked manufacturers to remove products containing this compound from the market because of an increased risk of hemorrhagic stroke. This action has caused a switch to the safer pseudoephedrine as the active component of such medications. Propose a reasonable method for converting a stockpile of 2-amino-1-phenylpropan-1-ol to pseudoephedrine.
5. (20 points, 4 each) Provide the major organic products of the following reactions

\[
\text{CH}_2\text{CH}_2\text{NH}_2 \xrightarrow{1) \text{CH}_3\text{I (excess), } \text{K}_2\text{CO}_3, \text{H}_2\text{O}} \xrightarrow{2) \text{Ag}_2\text{O}, \text{H}_2\text{O}} \xrightarrow{3) \Delta} \text{CH}_2\text{CH}_2\text{Cl}
\]

\[
\text{CH}_2\text{CH}_2\text{OH} \xrightarrow{1) \text{PBr}_3, \text{Br}_2} \xrightarrow{2) \text{H}_2\text{O}} \text{CH}_2\text{CH}_2\text{Br}
\]

\[
\text{CH}_2\text{CH}_2\text{Br} \xrightarrow{1) \text{NaN}_3} \xrightarrow{2) \text{LiAlH}_4, \text{THF}} \xrightarrow{3) \text{H}_2\text{O}} \text{CH}_2\text{CH}_2\text{CH}_2\text{OH}
\]

\[
\text{CH}_2\text{CH}_2\text{CH}_2\text{O} + \text{C}_6\text{H}_5\text{CH} = \xrightarrow{\text{NaOCH}_2\text{CH}_3, \text{CH}_3\text{CH}_2\text{OH}}
\]

\[
\text{CH}_2\text{CH}_2\text{CN} \xrightarrow{1) \text{LDA, THF}} \xrightarrow{2) \text{CH}_2\text{CH}_2\text{Br}}
\]

6. (16 points, 4 each) Fill in the missing reagents. Most of these transformations can be accomplished in only one step.

\[
\text{CH}_3\text{CH}_2\text{CHO} \xrightarrow{} \text{CH}_3\text{CH}_2\text{CH} = \text{Cl}
\]
7. (15 points, 5 each) Complete the following short syntheses by providing reagents over arrows and intermediate compounds in the boxes. All can be completed in two or three steps.
8. (8 points) Compound A, found in fresh cream, has a molecular formula of \( \text{C}_4\text{H}_8\text{O}_2 \). Compound A can be converted to compound B upon churning. Compound B gives butter its yellow color and characteristic odor and has the molecular formula \( \text{C}_4\text{H}_6\text{O}_2 \). From the \( ^1\text{H} \) NMR data listed below, determine the structures of A and B and place your final answers in the appropriate box.

<table>
<thead>
<tr>
<th>Compound A</th>
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<th>Compound B</th>
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<tbody>
<tr>
<td>( \delta 1.36 )</td>
<td>3H singlet</td>
<td>( \delta 2.29 )</td>
</tr>
<tr>
<td>( \delta 2.18 )</td>
<td>3H singlet</td>
<td>singlet</td>
</tr>
<tr>
<td>( \delta 3.73 )</td>
<td>1H broad singlet</td>
<td></td>
</tr>
<tr>
<td>( \delta 4.22 )</td>
<td>1H quartet</td>
<td></td>
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</table>

A

B
9. (6 points) Some reactions generate different products based on the reaction conditions. We talked about reactions that could give thermodynamic versus kinetic products. Provide a generic reaction energy diagram that shows how the thermodynamic energy curve differs from the kinetic energy curve. (Draw both reaction pathways on the same diagram and clearly indicate which one is which.) Point out the most important features of your energy curve. You do NOT need to include a specific reaction or any chemical structures.

10. (8 points) Starting from benzene and any other reagents you need, provide a synthesis for \( m \)-chlorophenol.
11. (12 points) Provide the necessary reagents for the following conversion. More than one step will be required. In addition to the given starting material, you may use any organic reagents of 3 carbons or less and any inorganic reagents you need. You must make any organometallic reagents and ylides if you plan to use them. You are strongly encouraged to show the product of each step so that partial credit can be awarded when appropriate.
12. (10 points) Provide a complete electron-pushing mechanism for the following reaction sequence. No other reagents are present, though you may assume reagents are present in excess, if needed. Show byproducts as they are formed. Clearly indicate which steps are reversible and which are not. For this problem ONLY, you MAY simply write P.T. over the reaction arrow for proton transfer steps in which you wish to protonate one portion of the molecule and deprotonate another.

\[
\begin{align*}
\text{1) CH}_3\text{NH}_2 \\
\text{2) CH}_3\text{OH, CH}_3\text{ONa} \\
\text{3) cold, dilute H}_2\text{O}^+ \\
\end{align*}
\]
13. (10 points) Provide a complete electron-pushing mechanism for the following reaction. Clearly indicate each step of the reaction (including any proton transfers).