DO NOT OPEN THE EXAM UNTIL INSTRUCTED

Exam 3

Directions:

Please check the exam to be sure there are 8 non-blank pages including the title page. Read all questions and directions carefully before entering answers.

GOOD LUCK
I. (30) In the space provided place the letter of the response which best answers or completes the statement.

A 1.

B 2.

B 3.

D 4.

D 5.

A 6.

D 7.

D 8.

A 9.

B 10.

Total _____
II. (15) Provide names (IUPAC or common) or structures for the following:

<table>
<thead>
<tr>
<th>Structure</th>
<th>Name</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1.png" alt="Structure" /></td>
<td>4-methyl-3-phenylpentanal</td>
</tr>
<tr>
<td><img src="image2.png" alt="Structure" /></td>
<td>3-buten-2-one methylvinylketone</td>
</tr>
<tr>
<td><img src="image3.png" alt="Structure" /></td>
<td>trans-3-chlorocyclobutanecarbaldehyde</td>
</tr>
<tr>
<td><img src="image4.png" alt="Structure" /></td>
<td>4-bromo-2-cyclopentenone</td>
</tr>
<tr>
<td><img src="image5.png" alt="Structure" /></td>
<td>E-4-chloro-3-butenal</td>
</tr>
</tbody>
</table>
III. (20) Draw the structure of the major product(s) or the reagents/conditions required to perform the following:

1. Treatment of a secondary alcohol with 
   - K$_2$Cr$_2$O$_7$, H$_2$SO$_4$, 
   - acetone 
   - or 
   - H$_2$CrO$_4$ 
   - acetic acid

2. Reaction of 2-pentanol with LDA followed by methyl bromide.

3. Addition of HOCH$_2$CH$_2$OH to a ketone with acid catalysis.

4. Error in structure: Reaction of (CH$_3$)$_3$CCH$_2$Br with Br$_2$ in acetic acid.

5. Treatment of an aromatic ketone with NaOH and water.
IV. (15) Provide explanations as requested:

(5) Explain the fact that, although hemiacetal formation between methanol and cyclohexanone is thermodynamically disfavored, addition of methanol to cyclopropanone goes essentially to completion:

\[
\text{H}_3\text{C} \quad \begin{array}{c}
\text{C} \\
\uparrow \\
\text{CH}_3
\end{array} \quad \text{+ CH}_3\text{OH} \quad \longrightarrow \quad \text{HO} \quad \begin{array}{c}
\text{C} \\
\uparrow \\
\text{OCH}_3
\end{array}
\]

The sp\(^2\) hybridized carbon of the carbonyl in cyclopropenone introduces considerable additional ring strain in an already very strained system. Addition of methanol to form the hemiacetal, normally thermodynamically less stable in acyclic systems, produces a more stable hemiacetal because it reduces the bond angle requirement from 120° (sp\(^2\)) to 109.5° (sp\(^3\)).

(5) It has been observed that methyl vinyl ketone undergoes conjugate addition with enolate nucleophiles like cyclohexanone enolate. Explain or show what conjugate addition is and explain why this is a likely mode of reaction.

The enolate adds to the vinyl carbon rather than the carbonyl carbon because a resonance stabilized anion is formed.

(5) Arrange the labeled hydrogens in the following molecule in order of increasing acidity (least acidic first) and provide an explanation for your order.

|a|b|c| C < A < B  C is least acidic because it is an ordinary sp\(^3\) hybridized C-H bond that is not acidic. A and B are much more acidic because they are alpha to the carbonyl which will provide resonance stabilization of the anion formed by ionization. B is most acidic because one of the resonance structures exhibits double bond character which is more highly substituted than A. |
V. (20) Answer the questions on any two of the following three pages. Write ‘OMIT’ through the page you wish omitted. Your answers must be clear and complete in order to receive complete credit. A well drawn picture is frequently worth a thousand words.

1. Formulate a complete stepwise mechanism for the following reaction: In order to receive full credit you must use proper electron arrow pushing notation, clearly label all charged species and include non-bonding electrons.
2. Provide a synthesis of the following molecule (in several steps) from the indicated starting material: you may use any other required inorganic or organic materials.

Other schemes will work as well.
3. Describe how you would prepare the following molecule using an aldol condensation: