DO NOT OPEN THE EXAM UNTIL INSTRUCTED

Exam 4

Directions:

Please check the exam to be sure there are 9 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.

B 1.

E 2.

A 3.

C 4.

C 5.

C 6.

E 7.

C 8.

B 9.

A 10.
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="结构图" /></td>
<td>2-ethyl-3-butenoic acid</td>
</tr>
<tr>
<td><img src="image2.png" alt="结构图" /></td>
<td>E-2-bromo-3,4-dimethyl-2-pentenoic acid</td>
</tr>
<tr>
<td><img src="image3.png" alt="结构图" /></td>
<td>Propyl propanoate</td>
</tr>
<tr>
<td><img src="image4.png" alt="结构图" /></td>
<td>2-methylhexanenitrile</td>
</tr>
<tr>
<td><img src="image5.png" alt="结构图" /></td>
<td>3-methylbutanoyl iodide</td>
</tr>
</tbody>
</table>
III. (20) Draw the structure of the major product(s) or the reagents/conditions required to perform the following:

\[
\text{C}_8\text{H}_{18}\text{NH}_2 + \text{ClCCH}_3 \rightarrow \text{C}_8\text{H}_{17}\text{NHCH}_3
\]

draw the rest of the product

\[
\left(\text{C}_8\text{H}_{18}\right)\text{CuLi} + \text{OCl}\text{C}\text{CH}_2\text{CH}_2\text{Cl} \rightarrow \text{C}_8\text{H}_{18}\text{COCl}
\]

1) Mg, Et\text{O}_2
2) CO\text{}_2
3) H\text{}_3\text{O}^+

or
1) NaCN, DMSO
2) H\text{}_2\text{O}, H^+

\[
\text{C}_8\text{H}_{18}\text{Br} \left[\begin{array}{c}
\text{OClCCH}_3 \\
\text{H}_3\text{O}^+
\end{array}\right] \rightarrow \text{C}_8\text{H}_{18}\text{CO}_2\text{H}
\]

hint: two steps

\[
\text{CH}_3\text{C}=\text{O} + \text{NaHCO}_3
\]
\[
\rightarrow \text{CH}_3\text{C}=\text{O}^-\text{Na}^+ + \text{CO}_2 + \text{H}_2\text{O}
\]

\[
\text{CH}_3\text{O} \quad \text{diisobutylalane (DIBAL)} \quad \text{CH}_3\text{O} \\
\text{H}_3\text{C}-\text{C}=\text{C}-\text{N}\ \text{CH}_3 \quad -78 \, ^\circ\text{C}, \text{THF} \quad \text{H}_3\text{C}-\text{C}=\text{C}-\text{H}
\]
IV. (15) Provide explanations as requested:

(5) The following compounds may form hydrogen ion by the following equilibria:

\[
\begin{align*}
\text{H}_3\text{C} & \text{C} = \text{NH}_2 & \text{H}_3\text{C} & \text{C} = \text{NH} & + \text{H}^+ \\
\text{H}_3\text{C} & \text{C} = \text{OH} & \text{H}_3\text{C} & \text{C} = \text{O} & + \text{H}^+
\end{align*}
\]

Identify which of the two hydrogen sites are most acidic and briefly explain drawing resonance structures to support your hypothesis.
Both anions above are resonance stabilized which will increase the acidity of the respective hydrogen. However, the lower anion (carboxylate anion) distributes the negative charge over two more electronegative oxygen atoms while the upper amide anion places charge on a less electronegative nitrogen atom. The carboxylic acid is more acidic as a result.

(5) Explain why there is hindered rotation about the carbon-nitrogen single bond in amides (like \text{N,N-} \text{dimethylformamide below}) and peptides.

\[
\begin{align*}
\text{H}_3\text{C} & \text{C} = \text{NH}_3 & \text{H}_3\text{C} & \text{C} = \text{NCH}_3 \\
\text{H}_3\text{C} & \text{C} = \text{NH}_3 & \text{H}_3\text{C} & \text{C} = \text{NCH}_3
\end{align*}
\]

The resonance interaction of the non-bonding electrons on the nitrogen with the carbonyl causes the C-N bond to have double bond character which causes hindered rotation since the interaction cannot occur unless the system is coplanar.

(5) From the mass spectrum on the following page deduce what other elements are present besides carbon and hydrogen. Provide a brief explanation for the additional elements you believe to be present.

The odd molecular ion (M$^+$ = 171) indicates that an odd number of nitrogen atoms are likely present. The approximately equal intensity M$^+$ and M + 2 ions indicate that bromine is present.
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. Draw a detailed mechanism indicating non-bonding electrons, charges and resonance structures for the following reaction: (your mechanism must keep track of the $^{18}$O label)

$$\text{CH}_3\text{CH}_2^{18}\text{OH} + \text{CH}_3\text{CH}_2\text{CO}_2\text{H} \xrightarrow{\text{H}^+} \text{H}_2\text{O} + \text{CH}_3\text{CH}_2\text{CO}_2\text{CH}_2\text{CH}_3$$

oxygen-18 label intentionally omitted - you must indicate where it is located in the products.
2. Outline a synthesis of 2-aminobutanoic acid from butanoic acid and any other necessary inorganic or organic reagents or solvents:

\[
\text{CH}_3\text{CH}_2\text{CHCO}_2\text{H} + \text{Br}_2/\text{cat. P} \rightarrow \text{CH}_3\text{CH}_2\text{CHCO}_2\text{H} + \text{Br}
\]

\[
\text{CH}_3\text{CH}_2\text{CHCO}_2\text{H} + \text{NH}_3 \rightarrow \text{CH}_3\text{CH}_2\text{CHCO}_2\text{H} + \text{NH}_2
\]
3. Formulate a mechanism for the reaction of acetyl chloride (ethanoyl chloride) with 1-propanol to produce propyl acetate (propyl ethanoate).