1. (a) (6 points) Why are the CH₂ protons of 3-pentanone so much more acidic than its CH₃ protons? Draw two resonance structures for the enolate anion of 3-pentanone and use these structures in your explanation. Clearly indicate all appropriate π-bonds, lone pairs of electrons, and formal charges.

\[
\text{H}_3\text{C}-\text{C}^\text{=O} \quad \text{strong base} \quad \rightarrow \quad \text{CH}_3\text{C}_2\text{H}_4\text{CH}_3
\]

The enolate anion is stabilized by the resonance structure II which places negative charge on the less electronegative oxygen. This is more stable than the localized carbamion.

(b) (6 points) The basic amino acid arginine has the guanidine side group shown below. Which nitrogen of guanidine gets protonated upon addition of acid? Draw three resonance structures for protonated guanidine. Clearly indicate all appropriate π-bonds, lone pairs of electrons, and formal charges.

\[
\text{R} = \text{H}
\]

pKa = 12.5

2. (4 points) Circle the hydrogens that would be replaced by deuterium when the following ketone was treated with NaOD in D₂O.
3. Draw the structures of the following compounds. **Explicitly show all carbons and hydrogens.**

(a) (3 points) benzyl acetate (jasmine odor)

(b) (4 points) (R)-2-methylhexanoic acid (clearly show stereochemistry)

(c) (3 points) glycerol (hint, this compound is obtained from hydrolysis of fats)

4. (9 points) Draw the structure of a specific example of three (and only three) of the following types of compounds: a fat, a wax, a soap, a dipeptide, a *trans* fatty acid, a lactone, a steroid, a terpene, an aromatic nitrogen heterocycle, a phospholipid.

(a) Type: **Fat**

(b) Type: **Soap**

(c) Type: **Steroid**
5. (6 points) The pKa's of the protonated amino acid aspartic acid are 2.1, 3.9, and 9.8. Draw the major species present at pH = 7 and at pH = 13.

6. (12 points) Azadirachtin is a natural insecticide isolated from the seeds of the neem tree found in India and Burma. The compound zaps pest species but leaves pollinating insects and mammals unharmed. Examine the molecule closely and note the wide range of functional groups present and the large number of asymmetric carbons present in the molecule.

Azadirachtin has 4 ester functional groups. Draw a BOX around one ester.

Draw a TRIANGLE around an epoxide functional group.

Draw a DIAMOND around an acetal functional group

CIRCLE a hemiacetal (or hemiketal) functional group.

Azadirachtin has 16 asymmetric carbon atoms.
7. We have seen many reactions that link two organic molecules. Indicate the starting materials needed to make the following compounds.

(a) (6 points) A Grignard synthesis of an alcohol. A Grignard reagent is an organomagnesium halide.

(b) (4 points) An aldol condensation:

(c) (6 points) Ester formation:
8. Write the expected products of the following hydrolysis reactions.

(a) (5 points)

\[
\begin{array}{c}
\text{H}^+ \\
\text{H}_2\text{O}
\end{array}
\xrightarrow{\text{H}^+} 
\begin{array}{c}
\text{H}^+ \\
\text{H}_2\text{O}
\end{array}
\]

(b) (6 points)

\[
\begin{array}{c}
\text{NaOH} \\
\text{H}_2\text{O} \\
100 \degree \text{C}
\end{array}
\xrightarrow{\text{NaOH}} 
\begin{array}{c}
\text{H}^+ \\
\text{H}_2\text{O} \\
100 \degree \text{C}
\end{array}
\]

(c) (6 points)

\[
\begin{array}{c}
\text{NaOH} \\
\text{H}_2\text{O} \\
100 \degree \text{C}
\end{array}
\xrightarrow{\text{NaOH}} 
\begin{array}{c}
\text{H}^+ \\
\text{H}_2\text{O} \\
100 \degree \text{C}
\end{array}
\]

9. (a) (4 points) **CIRCLE** the most acidic compound shown below; draw a **BOX** around the least acidic compound.

\[
\begin{array}{c}
\text{CH}_3 \\
\text{H}_3\text{C} \\
\text{H}_2\text{C} \\
\text{H}_3\text{C}
\end{array}
\]
(b) (4 points) **CIRCLE** the most basic compound shown below; draw a **BOX** around the least basic compound.

```
<table>
<thead>
<tr>
<th>NOT</th>
</tr>
</thead>
<tbody>
<tr>
<td>COVERED</td>
</tr>
<tr>
<td>YET</td>
</tr>
</tbody>
</table>
```

9. (8 points) Write a mechanism for the reaction of acetic anhydride with methanol. Show all intermediates and use "electron pushing arrows" to show how each intermediate is converted to the next.

```
\( \text{CH}_3\text{CO}_2\text{CH}_3 + \text{CH}_3\text{OH} \rightarrow \text{CH}_3\text{COOCH}_3 + \text{CH}_3\text{CO}_2\text{H} \)
```

```
\[ \begin{array}{c}
\text{CH}_3\text{CO}_2\text{CH}_3 + \text{CH}_3\text{OH} \rightarrow \text{CH}_3\text{COOCH}_3 + \text{CH}_3\text{CO}_2\text{H} \\
\text{CH}_3\text{COOCH}_3 + \text{H}^+ \rightarrow \text{CH}_3\text{CO}_2\text{H} + \text{CH}_3\text{OH} \\
\text{CH}_3\text{CO}_2\text{H} \rightarrow \text{CH}_3\text{CO}_2\text{CH}_3 + \text{H}^+ \\
\text{CH}_3\text{CO}_2\text{CH}_3 + \text{CH}_3\text{OH} \rightarrow \text{CH}_3\text{COOCH}_3 + \text{CH}_3\text{CO}_2\text{H} \\
\end{array} \]
```

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**Circle the name of your discussion TA**

1. (Salwa Salah)
2. (Ramon Sanchez)
3. (Eric Benedict)
4. (Kim Smith)
5. (Nate Bowling)

**TOTAL**