51A Final Exam Review Session Key

1. Answer the following questions about octocrylene, a common sunscreen component.
   a. What is the hybridization of each C atom?
   b. How many lone pairs does octocrylene contain?
   c. What is the geometry around each C atom?
   d. Draw two additional resonance structures.
   e. Label all polar bonds.

![Octocrylene structure](attachment:octocrylene.png)

(Smith 6th Ed., Ch. 1, #77)
The number of electron groups around an atom determines both its geometry and hybridization:

<table>
<thead>
<tr>
<th>Number of groups</th>
<th>Geometry</th>
<th>Bond angle (°)</th>
<th>Hybridization</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>linear</td>
<td>180</td>
<td>sp</td>
</tr>
<tr>
<td>3</td>
<td>trigonal planar</td>
<td>120</td>
<td>sp²</td>
</tr>
<tr>
<td>4</td>
<td>tetrahedral</td>
<td>109.5</td>
<td>sp³</td>
</tr>
</tbody>
</table>

a. C’s labeled with a blue circle = sp³
   C’s labeled with a green circle = sp²
   C’s labeled with a red circle = sp

b. In their neutral states, oxygen has two lone pairs and nitrogen has one lone pair.
   Therefore, octocrylène has 5 lone pairs in total.

c. C’s labeled with a blue circle = tetrahedral
   C’s labeled with a green circle = linear
   C’s labeled with a red circle = trigonal planar
e. All C-O bonds and the C≡N bond are polar. A polar bond results when two atoms of different electronegativity values are bonded together. Whenever C is bonded to N, O, or any halogen, the bond is polar.
2. Use the observed bond lengths to answer each question.
   (a) Why is bond [1] longer than bond [2] (143 pm versus 136 pm)?
   (b) Why are bonds [3] and [4] equal in length (127 pm), and shorter than bond [2]?

\[ \text{H}_3\text{C} - \text{OH} \quad \text{[1]} \quad \text{H}_3\text{C} - \text{C} - \text{OH} \quad \text{[2]} \quad \text{H}_3\text{C} - \text{C} - \text{O} \quad \text{[3]} \quad \text{H}_3\text{C} - \text{C} - \text{O}^{-} \quad \text{[4]} \]

**Answer:**

a. 
\[
\begin{align*}
\text{H}_3\text{C} - \text{OH} \quad &\quad \text{sp}^3 \\
\end{align*}
\]

**25% s-character**

The lower percent s-character makes this bond longer.

b. 
\[
\begin{align*}
\text{H}_3\text{C} - \text{C} - \text{O}^{-} \quad &\quad \text{[3]} \\
\text{H}_3\text{C} - \text{C} - \text{O}^{-} \quad &\quad \text{[4]} \\
\end{align*}
\]

**Two resonance structures**

Bonds [3] and [4] are both equivalent in length, because the anion is resonance stabilized, and the C–O bond of the hybrid is a composite of one single bond and one double bond. Both resonance structures contribute equally to the hybrid. Because each C–O bond in the hybrid has partial double bond character, it is shorter than the C–O bond labeled [2].
3. Label the three most acidic hydrogen atoms in lactic acid, CH₃CH(OH)CO₂H, and rank them in order of decreasing acidity. Explain your reasoning.

(Smith 6th Ed., Ch. 1, #83)

**ANSWER:**

Immediately we can eliminate the H’s of the CH₃ group; they are bonded to an sp³ hybridized C and the conjugate base formed by their removal is not resonance stabilized - this makes them the least acidic protons of lactic acid.
4. Synthadotin is a promising anticancer drug in clinical trials.
a. Identify the functional groups.
b. At which sites can synthadotin hydrogen bond to another molecule like itself?
c. Label two nucleophilic sites.
d. Label two electrophilic sites.
e. What product is formed when synthadotin is treated with HCl?

(Smith 6th Ed., Ch. 3, #62)

**ANSWER:**

![Diagram of synthadotin with labels for amides and amines]

a. R<sub>2</sub> and R<sub>3</sub> can be hydrogen or alkyl group

![Diagram of amide structure]

![Diagram of amine structure]
b. Synthadotin can hydrogen bond to itself at the N-H sites (highlighted in red). Hydrogen bonding occurs when a hydrogen atom bonded to O or N is electrostatically attracted to a lone pair of electrons on an O or N atom in another molecule.

c. The nucleophilic sites are any O or N atom with lone pairs. Nucleophiles are electron-rich and can donate an electron pair to an electrophile.

d. The electrophilic sites are any carbonyl C’s that have a double bond to oxygen. Electrophiles are electron-deficient and can accept an electron pair from a nucleophile.

e. When synthadotin is treated with HCl, the amine N (the most basic atom) is protonated.
5. For each conformation below:
   a. Label each OH, Br, and CH₃ as axial or equatorial.
   b. Classify each conformation as cis or trans.
   c. Translate each structure into a representation with a hexagonal six-membered ring, and wedges and dashed wedges for groups above and below the ring.
   d. Draw the second possible chair conformation for each compound.

   ![Chemical structures](image)

   (Smith 6th Ed., Ch. 3, #62)

   **ANSWER:**
1. **Hexagonal Representation**

Trans: One OH group is directed upward; one downward

2. **Hexagonal Representation**

Cis: Both Br & Methyl Groups pointed upwards

3. **Hexagonal Representation**

Trans: One OH group directed upward; one downward

Note: When converting charts to hexagonal rings, you can begin numbering at any point on the hexagonal ring as long as you are consistent with the direction you count on both the chair and hexagonal ring.
6. For the compound drawn below:
   a. Draw representations for the cis and trans isomers using a hexagon for the six-membered ring, and wedges and dashed wedges for substituents.
   b. Draw the two possible chair conformations for the cis isomer. Which conformation, if either, is more stable?
   c. Draw the two possible chair conformations for the trans isomer. Which conformation, if either, is more stable?
   d. Which isomer, cis or trans, is more stable and why?

(Smith 6th Ed., Ch. 4, #55)

**ANSWER:**

a.

![cis isomer](image1)

![trans isomer](image2)

NOTE: Other possible isomers can be drawn

b.

![Chair conformation conversion](image3)

more stable because bulkier group is equatorial
c. The trans isomer is more stable than the cis isomer because one of its conformations has both substituents on the equatorial position, leading to less steric hindrance between atoms.

more stable because both groups are equatorial
7. Draw all possible stereoisomers for each compound. Label pairs of enantiomers and diastereomers. Label any meso compound. (Only do a couple of these, do letter d).

a. 

\[\text{OH} \quad \text{CH}_3 \quad \text{CH}_3 \]

b. 

\[\text{CH}_3 \quad \text{CH}_3 \quad \text{Cl} \quad \text{Br}\]

c. 

\[\text{Cyclic structure} \]

d. 

\[\text{Cyclic structure} \]

(Smith 6th Ed., Ch. 5, #58)

**ANSWER:**
C is a meso compound; its mirror image is identical to itself.

Pair of enantiomers: A and B
Pairs of diastereomers: A and C, B and C

Pair of enantiomers: A and B, C and D
Pairs of diastereomers: A and C, A and D, B and C, B and D
8. The $[\alpha]$ of pure quinine, antimalarial drug, is -165.
a. Calculate the ee of a solution with the following [α] values: −50, −83, and −120.
b. For each ee, calculate the percent of each enantiomer present.
c. What is [α] for the enantiomer of quinine?
d. If a solution contains 80% quinine and 20% of its enantiomer, what is the ee of the solution?
e. What is [α] for the solution described in part (d)?

(Smith 6th Ed., Ch. 5, #68)

ANSWER:
\[ \begin{align*}
\text{quinine} & \quad \text{quinine's enantiomer} = B \\
\text{a. } & \quad \frac{-50}{-165} \times 100\% = 30\% \text{ ee} \\
\text{b. } & \quad 30\% \text{ ee} = 30\% \text{ excess one compound (A)} \\
& \quad \text{remaining } 70\% = \text{mixture of 2 compounds (35\% each A and B)} \\
& \quad \text{Amount of A} = 30 \div 35 = 65\% \\
& \quad \text{Amount of B} = 35\% \\
\text{c. } & \quad \frac{-83}{-165} \times 100\% = 50\% \text{ ee} \\
\text{d. } & \quad 50\% \text{ ee} = 50\% \text{ excess one compound (A)} \\
& \quad \text{remaining } 50\% = \text{mixture of 2 compounds (25\% each A and B)} \\
& \quad \text{Amount of A} = 50 \div 25 = 75\% \\
& \quad \text{Amount of B} = 25\% \\
\text{e. } & \quad \frac{-120}{-165} \times 100\% = 73\% \text{ ee} \\
\text{f. } & \quad 73\% \text{ ee} = 75\% \text{ excess one compound (A)} \\
& \quad \text{remaining } 27\% = \text{mixture of 2 compounds (13.5\% each A and B)} \\
& \quad \text{Amount of A} = 73 \div 13.5 = 86.5\% \\
& \quad \text{Amount of B} = 13.5\% \\
\text{g. } & \quad [\alpha] = +165 \\
\text{h. } & \quad 80\% - 20\% = 60\% \text{ ee} \\
\text{i. } & \quad 60\% = \frac{[\alpha] \text{ mixture}}{-165} \times 100\% \\
\text{j. } & \quad [\alpha] \text{ mixture} = -99
\end{align*} \]
8. Identify the structures of isomers E and F (molecular formula C₄H₈O₂). Relative areas are given above each signal.

f. IR spectrum for E:

![IR spectrum for E]

![1H NMR of E]

g. IR spectrum for F:
(Smith 6th Ed., C.64)
**ANSWER:**

a. **Compound E:**

**C₄H₉O₂:**

1 degree of unsaturation

IR absorption at 1743 cm⁻¹: C=O

**NMR data:**

Hₐ: quartet at 4.1 (2 H)
Hₖ: singlet at 2.0 (3 H)
Hₜ: triplet at 1.4 (3 H)

![Diagram of compound E]

b. **Compound F:**

**C₄H₉O₂:**

1 degree of unsaturation

IR absorption at 1730 cm⁻¹: C=O

**NMR data:**

Hₐ: singlet at 4.1 (2 H)
Hₖ: singlet at 3.4 (3 H)
Hₜ: singlet at 2.1 (3 H)

![Diagram of compound F]

**A.**

Ha has three neighboring adjacent H of equal environment; N+1 = quartet.

Hb is a singlet with 3H so it must be adjacent to the ester.

Hc must be furthest from the O, and additionally, because it is a triplet, must go with the quartet group as an ethyl group via patterns.

**B.**

Note the difference. Ha is relatively the same shift, but now is a singlet, meaning it is now bounded by an O and a ketone given that it contains only 2 H’s so much be participating in both bonds. Hb and Hc are singlets with 3H integration, but one is adjacent to a ketone and one adjacent to an O. The H adjacent to an O has a higher shift than that adjacent to a ketone due to the increased inductive deshielding effect. Thus, Hb corresponds to the terminal methyl group of the ether, and Hc is the methyl group adjacent to the ketone.
9. Identify the structures of isomers H and I (molecular formula $\text{C}_8\text{H}_{11}\text{N}$).

a. IR spectrum for Compound H:

![IR spectrum for Compound H]

b. $^1\text{H}$ NMR for Compound H:

![$^1\text{H}$ NMR for Compound H]

c. IR spectrum for Compound I:

![IR spectrum for Compound I]
d. $^1$H NMR for Compound I:
a. **Compound H:**

C₈H₈N:

4 degrees of unsaturation

IR absorptions at 3365 cm⁻¹: N–H
3284 cm⁻¹: N–H
3026 cm⁻¹: Csp²–H
2932 cm⁻¹: Csp³–H
1603 cm⁻¹: due to benzene
1497 cm⁻¹: due to benzene

NMR data:

multiplet at 7.2–7.4 ppm, 5 H on a benzene ring
H₂: triplet at 2.9 ppm, 2 H, split by 2 H's
H₃: triplet at 2.8 ppm, 2 H, split by 2 H's
H₄: singlet at 1.1 ppm, 2 H, no splitting (on NH₂)

b. **Compound I:**

C₈H₈N:

4 degrees of unsaturation

IR absorptions at 3367 cm⁻¹: N–H
3286 cm⁻¹: N–H
3027 cm⁻¹: Csp²–H
2962 cm⁻¹: Csp³–H
1604 cm⁻¹: due to benzene
1492 cm⁻¹: due to benzene

NMR data:

multiplet at 7.2–7.4 ppm, 5 H on a benzene ring
H₆: quartet at 4.1 ppm, 1 H, split by 3 H's
H₇: singlet at 1.45 ppm, 2 H, no splitting (NH₂)
H₈: doublet at 1.4 ppm, 3 H, split by 1 H
9. The IR (> 1500 cm⁻¹ only) and 1H NMR spectra of Q [molecular formula C₅H₁₀O] are given below. What is the structure of Q?

**ANSWER:**

\[ \text{C}_5\text{H}_{10}\text{O}: 1 \text{ Degree of Unsaturation} \]

IR Data:

- IR Absorption at roughly 1700 cm⁻¹ = C=O

H NMR Data:

- \( \text{H}_a \): doublet at 1.1 ppm, 2CH₃ groups split by 1H
- \( \text{H}_b \): singlet at 2.1 ppm, CH₃ group
- \( \text{H}_c \): septet at 2.6 ppm, 1H split by 6 H’s

Thought Process: Use Clues to Figure Out the Structure

**Clue #1: Unsaturation Number**
• There is only one degree of unsaturation with C and H and O. This indicates that the 1 degree likely comes from the O interacting with the C in a double bond. This is likely a chain rather than a ring based on an unsaturation number. *Two degrees of unsaturation is equivalent to 2 double bonds, 1 ring and 1 double bond, 2 rings, or 1 triple bond.*

Clue #2: IR Absorption
• We have no -OH groups nor an aldehyde fermi doublet on the IR, and can rule out any alkenes due to the lack of Csp² C-H bonds. In fact, given that there is an peak around 1700cm⁻¹ this indicates that the O is in fact involved in a double bond with C, which is where the one degree of unsaturation must come from, confirming our previous hypothesis, and that a ketone is present (not an aldehyde or an ether) and the fact that there is only one heteroatom precludes esters, amides, amines, etc.

Clue #3: H NMR Data
• At this point, we have a rough idea of the functional groups present on our molecule. Now it is a matter of how the hydrogens are distributed among the carbons. A doublet at 1.1ppm with 6 H’s on the integration alongside another septet signal at 2.6ppm that has an integration peak of 1 is an isopropyl pattern. The one H on the tertiary C of the isopropyl will be surrounded by 6 adjacent H’s of equivalent signal, and via N+1 rule this will visualize as a septet. Conversely, the two methyl groups on the isopropyl will be in identical environments and have equivalent signals and be surrounded by only one adjacent H on the tertiary C, which will make them a doublet. Finally, the singlet at 2.1 ppm of 3 H’s matches with the chemical shift of a methyl group.

Integrating the Data:
• Now, with all of the information we have gathered from these clues, we can begin to form what we think the structure may be. This is a dynamic process at times; feel free to propose certain structures and check back to see if you satisfy all data and maintain the parameters set with the molecular formula and unsaturation numbers (e.g. adding too many carbons, adding functional groups not seen, adding H’s in a way that don’t reflect splitting patterns, or creating rings that will extend the unsaturation number beyond what was calculated).
11. **ANSWER:**

An unknown Compound, Z, has the molecular formula, C$_7$H$_{14}$O$_2$. Complete the following:

1. Calculate the units of unsaturation

$$\text{Units of Unsaturation} = \frac{2(7) + 2 - 14}{2} = 1$$

2. For the IR, use arrows to point out important IR stretches. Label each arrow with the type of bond or functional group present

(Answer provided in IR spectrum)

3. For H NMR, fill out the chart given with chemical shifts, integration, splitting, # of adjacent H’s, and a partial structure that corresponds to each signal

(Answer provided in chart)

4. Combine all of this to provide a complete structure for the unknown compound.

Using what we have from the molecular formula, units of unsaturation, and IR we know we have a carbonyl compound with some alkyl chain. Since the IR shows no distinct O-H peak we can deduce that we likely have an ester. Combining this information with the NMR data, we get the following completed structure:

```
\begin{center}
\includegraphics[width=0.5\textwidth]{structure.png}
\end{center}
```

**IR:**

```
\begin{center}
\includegraphics[width=0.8\textwidth]{ir_spectrum.png}
\end{center}
```

**H$^1$ NMR:**
### $^1$HNMR signals:

<table>
<thead>
<tr>
<th>Chemical shift (ppm)</th>
<th>Integration (#H's)</th>
<th>Splitting</th>
<th># adjacent H's</th>
<th>Partial structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.9</td>
<td>3H</td>
<td>triplet</td>
<td>2H</td>
<td><img src="image" alt="Structure" /></td>
</tr>
<tr>
<td>1.2</td>
<td>6H</td>
<td>doublet</td>
<td>1H</td>
<td><img src="image" alt="Structure" /></td>
</tr>
<tr>
<td>1.7</td>
<td>2H</td>
<td>sextet</td>
<td>5H</td>
<td><img src="image" alt="Structure" /></td>
</tr>
<tr>
<td>2.3</td>
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<td>triplet</td>
<td>2H</td>
<td><img src="image" alt="Structure" /></td>
</tr>
<tr>
<td>5.0</td>
<td>1H</td>
<td>septet</td>
<td>6H</td>
<td><img src="image" alt="Structure" /></td>
</tr>
</tbody>
</table>