Final Review Key

Spectroscopy Practice:

Quizlet for IR stretches and NMR chemical shifts:
https://quizlet.com/379505269/o-chem-lab-flash-cards/

1. Samantha: Draw the resonance structures of the molecule below.

a. Circle the structure that contributes the most to resonance. Box the structure that contributes the least. Explain your choices.

The original molecule will be the greatest contributor to the hybrid structure because there are no formal charges. The second structure is the least because the positive charge is on the carbon, which is right next to the oxygen with a negative which is electron withdrawing, but the carbocation is electron-deficient, destabilizing the molecule.

b. Draw the hybrid structure of the molecule.
2. Samantha: List the hybridization and geometry of each atom indicated by an arrow.

![Image of molecule with hybridization and geometry labels](image)

- sp$^3$; tetrahedral
- sp$^2$; trigonal planar

a. Would this molecule be relatively soluble in a polar solvent? Why or why not?

Yes, following the 5 carbons to 1 polar and hydrogen bond-capable polar group, this molecule is soluble in a polar solvent. 10:2 carbon to polar functional group ratio.

b. Which of the following functional groups is present in this molecule?

A) Nitro  
B) Amine  
C) Hydroxyl  
D) Amide  
E) Thiol

3. Samantha: Draw the products of each reaction. Label the nucleophile, electrophile, Lewis Acid base/acid, and/or Bronsted-Lowry base/acid.

a.

![Image of reaction](image)
b.

\[
\text{CORRECTION: NOT a BL base because no proton was accepted}
\]

4. Samantha: Rank the following compounds from lowest to highest boiling point and list the intermolecular forces of each.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Boiling Point</th>
<th>Intermolecular Forces</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 VDW</td>
<td></td>
<td>VDW</td>
</tr>
<tr>
<td>2 VDW</td>
<td></td>
<td>VDW</td>
</tr>
<tr>
<td>3 VDW</td>
<td></td>
<td>VDW, Dipole-Dipole</td>
</tr>
<tr>
<td>4 VDW</td>
<td></td>
<td>VDW, Dipole-Dipole, H-Bonding</td>
</tr>
</tbody>
</table>


a. Is this conformation eclipsed or staggered? **Staggered**

b. How many chiral centers are there? If there are any, label absolute configuration(s). 1; S
6. Samantha: Give the IUPAC name of the following molecule.

![Molecule Image]

1-cyclobutyl-4-isopropyl-7,7-dimethylnonane

7. Draw two chair conformations for the cyclohexane below and circle the more favorable conformation and explain why.

![Cyclohexane Image]

All the constituents are in the equatorial position in the second chair conformation, which reduces steric strain between the groups.

8. Samantha: Circle the most acidic proton in acetaminophen shown below. Explain your choice.

![Acetaminophen Image]

The hydroxyl proton is the most acidic because when considering elemental effects, oxygen is the most electronegative. PKa can also be taken into consideration; the hydroxyl is 16 while the amide is 25. Although the amide has resonance effects, atomic effects dominate.

9. Georgene: Label the molecules below as chiral, achiral, or meso:
   a. Chiral- draw mirror image and see that it isn’t superimposable
b. Achiral- no stereocenters

c. Meso- stereocenters with plane of symmetry

d. Meso

10. Georgene: Is the stereochemistry of each molecule correct? If not, label the correct stereochemistry.
   a. S (correct is R)
   b. 1 is S and 2 is S
11. Georgene: Identify the type of organic reaction and draw in the missing arrows:

a. Substitution

b. Elimination

c. Addition

d. Don’t have to draw these arrows but label what type of reaction it is: Oxidation
12. Georgene: A concerted reaction is where no intermediates are present. A stepwise reaction is where one or more reactive species will be present en route to the product.
   a. Reaction A in problem #1 is: concerted or stepwise
   b. Reaction C in problem #1 is: concerted or stepwise

13. Georgene: Rank the indicated bonds in order of increasing bond dissociation energy:

   ![C-Cl bonds with bond dissociation energies](image)

   1>3>2
   C-Cl bonds are shorter → stronger → higher bond dissociation energy

14. Georgene: Given each value, determine whether the starting material or product is favored at equilibrium.
   a. $K_{eq} = 0.5$
      - Favors starting material → when $K_{eq} < 1 = $ favors reactants
      - $K_{eq} = \frac{[\text{products}]}{[\text{reactants}]}$ (when you favor products, the fraction is greater than 1)
   b. $\Delta G^\circ = -100 \text{ kJ/mol}$
      - Favors product → when $\Delta G < 0 = $ favors products
      - When $\Delta G < 0$, that means the $\Delta H - T\Delta S < 0$ and because $T\Delta S$ is usually small, a $\Delta H$ being less than 0 means the reaction is exothermic, which favors products.
   c. $\Delta H^\circ = 8.0 \text{ kJ/mol}$
      - Favors starting material → when $\Delta H > 0 = $ favors reactants be $\Delta G \sim \Delta H$ ($T\Delta S$ is usually small) → $\Delta G = \Delta H - T\Delta S$

15. Georgene: Write out the rate equation for both reactions below:
   a. Rate = $k[1\text{-iodo-cyclohexane}][\text{OH}^-]$
1-iodo-cyclohexane is a 2° alkyl halide which undergoes SN2 mechanism (concerted)
b. Rate = k[1-iodo-1-methylcyclohexane]
The slow step in a stepwise reaction dominates the rate law.

1-iodo-1-methylcyclohexane is a 3° alkyl halide which undergoes SN1 (step-wise) →
carbocation formation

16. Georgene: Calculate the degree(s) of unsaturation for the following compounds:
Formula: \( \frac{1}{2} (2 + 2\#C - \#H + \#N - \#\text{Halogens}) \)
a. \( \text{CH}_3\text{COOH} = 1 \) (due to the C=O)

b. = 2 (due to the C=O and the ring)
c. \( \text{C}_5\text{H}_9\text{O}_2\text{F} = 1 \)

17. Georgene: Mass spectrometry is used to determine the molecular weight of compounds by analyzing the relative abundance of charged ions from a sample. The Nitrogen rule states that an odd # of Nitrogens results in an odd mass and an even # of Nitrogens results is an even mass.
a. Would this MW be odd or even? Even (0 Nitrogens = Even)

b. Would this MW be odd or even? Odd
18. Complete the following:  (Erinna)

19. How would you use HNMR to distinguish between the following pairs of compounds? Pick one signal for each set that could be used and write the appropriate chemical shift, splitting, and integration for each.

20.  
   a. Calculate the Degree of Unsaturation: \( \text{C}_4\text{H}_8\text{O}_2 \)  
      \[
      2C+2+N-X-H/2 \\
      2(4)+2+0-8/2 \\
      =1 \text{ pi bond or 1 ring}
      \]
b. Determine the structure of the following compound using the molecular formula, IR, and HNMR

21. Atropine is a drug that is extracted from deadly nightshade that is used in the treatment of bradycardia (low heart rate) and cardiac arrest. Most of the physiological effects are due to the L-enantiomer shown below.

\[ (-)\text{-Atropine} \]

\[ [\alpha]_D^{25} = -22^\circ \]
a. Calculate the \( \% ee \) of a solution with a specific rotation of \(-18.5^\circ\).

\[
\% ee: \quad \frac{\alpha}{[\alpha]} = \frac{-18.5^\circ}{-22} = 84.09\%
\]

b. What is the stereochemical composition of the sample in part b?

\[
\text{\%}(-): 92.05 \quad \text{\%}(+): 7.95\%
\]

\[
100 - 84.09 = 15.91 \\
15.91/2 = 7.955
\]

c. What is \([\alpha]_D^{25}\) for (+)-Atropine?

\[
[\alpha]_D = -22^\circ
\]

d. (4 points) What is the observed rotation for a solution of 0.50 g (+)-Atropine and 0.05g (-)-Atropine in 100 mL of methanol, using a 1 dm cell?

\[
\frac{\alpha}{C e} = \frac{[\alpha]_D C e}{22 (0.0459\text{ml})(1\text{dm})} = \frac{1.099^\circ}{0.0459}\text{ml}
\]

For extra NMR problems, visit this website:

https://www.chem.wisc.edu/areas/reich/handouts/NMR-Spectra/NMR-isomers-of-c4h6o2.pdf