Chapter 1

1. Use the following ball-and-stick model to answer the following questions. (1.36)

A. Draw a skeletal structure of carbidopa.
B. Determine the hybridization around each central atom.
C. What is the hybridization and geometry around each N atom?
D. How many polar bonds are present?

Solution:

A.

B.

C.
D. Polar bonds are bonds between 2 different atoms that have a difference in electronegativity of at least 0.5. Thus, all C-O, O-H, N-H, N-C bonds are polar bonds. There are 11 polar bonds in total.

2. Answer each question about L-dopa. (1.11)

A. Convert the structure into a Lewis structure.
B. What is the hybridization around each labelled atom?
C. Label 3 polar bonds.

Solution:
A. B.
C. If you labelled any of 3 of the C-O, O-H, N-H, C-N bonds, you would be correct.

Chapter 2
3. Label Lewis acid and base, then use curved arrow notation to show the movement of electron pairs. (2.32)
A.

\[
\begin{align*}
\text{BF}_3 & \quad + \quad \text{CH}_3\text{OCH}_3 \\
\rightarrow & \quad \text{BF}_2\text{OCH}_3
\end{align*}
\]

B.

\[
\begin{align*}
\text{CH}_3\text{CH}_2\text{CH}_3 & \quad + \quad \text{OH}^- \\
\rightarrow & \quad \text{CH}_3\text{CH}_2\text{OH}
\end{align*}
\]

Solution:
A.

\[
\begin{align*}
\text{electrophile} & \quad + \quad \text{Nucleophile} \\
\rightarrow & \quad \text{Product}
\end{align*}
\]
4. Rank the compounds in each group in order of increasing acidity. (2.25)

A.

B.

C.

Solution:

A. Elemental effect. Acidity increases across a row in a periodic table. Remember that all acids are electrophiles and thus like to accept electrons. Thus, the more electronegative, the more acidic something is. This is in accordance with the trend that acidity increase across a row in a periodic table.

B. More electronegative groups stabilize the conjugate base, making the acid stronger, thus, the presence of carbonyl carbon and hydroxyl and bromine make the last structure the most acidic. Structure on the left only has a hydroxyl group and nothing else, thus, it is
the least acidic. Also, we see that structures stabilized by resonance are more stable. Remember strong acids have a stable conjugate base. This is also why the sequence is arranged as such.

C.

Being a good acid means having acidic protons that are readily donated. This being said, the more electronegative the protons are bonded to, the more acidic that structure is. In the left structure, we can see that there are only C-H bonds, in the structure in the middle, we can see C-H and N-H bonds, and in the right structure, we have C-H and O-H bonds. Since electronegativity increases from C, N, to O, the structures’ acidity also increases in the same pattern.

**Chapter 3**

5. Identify all the functional groups in salinosporamide A, an anticancer agent. Then classify each alcohol, alkyl halide, amide, and amide as primary, secondary, and tertiary. (3.34)

**Solution:**
Amides: count the number of **carbons** directly attached to the **nitrogen**

- $\text{R}^+\text{C}^+\text{NH}_2$ (1 carbon directly attached)
- $\text{R}^+\text{C}^+\text{NH}_3^+$ (2 carbons)
- $\text{R}^+\text{C}^+\text{NH}_3^+$ (3 carbons)

Primary (1°) amide  Secondary (2°) amide  Tertiary (3°) amide

Alcohols: we count the number of **carbons** directly attached to the carbon bonded to the **OH**

- $\text{H}_2\text{O}$ (0 carbons)
- $\text{CH}_3\text{CH}_2\text{OH}$ (1 carbon directly attached)
- $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$ (2 carbons attached)
- $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$ (3 carbons attached)

Water  Primary (1°) alcohol  Secondary (2°) alcohol  Tertiary (3°) alcohol
6. Which compound in each pair has the higher boiling point? Which compound in each pair is more stable? Why? (3.3)

Solution:
Compound A and Compound D. Between A and B, we see that they are actually isomers (C6H14), so we have to look at the shape. We see that A is more expanded and less branched and thus has a larger surface area, making it capable of more VDW interactions, thus having a higher BP. Between C and D, we see that only D is capable of H-bonding, making D the obvious choice for having a higher BP due to the high strength of H-bonding.
A stable compound has strong interactions will have higher boiling points, thus, A would be more stable. D would be more stable.

**Chapter 4**

7. Draw both chair conformations for trans-1,3-dimethylcyclohexane. (4.3)

   Solution:

   ![Chair Conformations](image)

   Review of ring flip: Remember that axial becomes equatorial and equatorial becomes axial after a ring flip. However, trans structures remain trans structures and cis structures remain cis structures. Thus, an up stays up and a down stays down no matter the ring flip.

8. Give the IUPAC name for each compound:
   a.
   ![Compound A](image)
   b.
   ![Compound B](image)
Solution:

**Step 1**: Locate the longest chain, this becomes the parent chain, in the case of a cycloalkane, that is automatically the parent chain. In the case of multiple possibilities, select the parent chain that gives the most number of substituents.

**Step 2**: Label carbons from 1 to the number of carbons, make sure the number labelling results in the lowest numbers on substituents.

**Step 3**: Identify the names of substituents, such as methyl, isopropyl, and etc. Then arrange them into alphabetical order. Note: the prefix EXCEPT iso- is not considered in the alphabetical order arrangement.

**Step 4**: Put it all together.

A. 2,4-dimethylheptane
**Step 1**: Longest chain here is a heptane, thus, heptane is the parent chain.
**Step 2**: I labelled it above so that substituents would be on C2 and C4 instead of C4 and C6, which is wrong.
**Step 3**: We have 2 methyl groups, thus, we have dimethyl. Since we only have 2 substituents which happen to be the same, we don't need to arrange them in alphabetical order because we only have 1 thing.
**Step 4**: Put it all together, so the structure becomes 2,4-dimethylheptane.

B. 4-tert-butyl-4-methyloctane

C. 3-butyl-1,1-dimethylcyclohexane

D. 1,2,4-triethylcyclopentane

Chapter 5
A. Locate all the tetrahedral stereogenic centers

i. The green carbons correspond to stereogenic centers. Recall that tetrahedral carbon is a stereocenter when it has 4 different substituents attached to it.
B. Certain carbon double-double bonds can also be stereogenic centers. Explain how this can occur and then locate the three additional stereogenic centers in discodermolide.

![Discodermolide](image)

a.

i. Rotation of the noted C=C double bond above causes conformational change between trans and cis conformers. The rotation of terminal C=C double bond will not lead to conformational changes, thus it is not a stereogenic site. The double bond can only become a stereogenic site when the substituents on each end of the double bond are different from each other. For example, the rotation of the double bond on alkene shown below leads to different conformers, thus it acts as a stereogenic site,

![Examples](image)

C. Considering all the stereogenic centers, what is the maximum number of stereoisomers possible for discodermolide?
10. An acid-base reaction of R-sec-butylamide with a racemic mixture of 2-phenylpropanoic acid forms two products having different melting points and somewhat different solubilities. Draw the structure of these two products. Assign R and S to any stereogenic centers in the products. How are the two products related? Choose from enantiomers, diastereomers, constitutional isomers or not isomers.

The resulting products from acid-base extractions are diastereomers, thus they have varying melting points and may have different solubilities.

11. Racemic mixture of A and B are present with excess A. For the given ee values, calculate the percentage of each enantiomer present.

A. 90% ee
   a. 90% excess of A present, with remaining 10% of racemic mixture of A and B (5% each). In total there is 95% A and 5% B

B. 60% ee
   a. 60% excess of A present with remaining 40% of racemic mixture of A and B (20% each). In total, there is 80% A and 20% B

Chapter 6:
12. Write the rate equation for this reaction, assuming the first step is rate-determining.
   a. Rate = k[CH$_3$O$^-$][CH$_3$COCl]

B. If the concentration of alkoxide (CH$_3$O$^-$) were increased by 10 times what would happen to the rate of the reaction
   a. Alkoxide is in the rate equation, thus when its concentration is increased by 10 times, the rate of the reaction will increase by 10 times as well.

C. If the concentrations of both acetyl chloride and alkoxide were increased 10 times, what would happen to the rate of the reaction?
   a. Both alkoxide and acetyl chloride are in rate equation, thus if both concentrations increase by 10 times, the rate of reaction will increase by 10 x 10 or 100 times

D. Classify the conversion of acetyl chloride to methyl acetate as elimination, addition or substitution.
   a. Substitution, C-Cl bond is substituted with C-OCH$_3$ bond

13. Consider the following energy diagram for the overall reaction: (CH$_3$)$_3$COH + HI -> (CH$_3$)$_3$Cl + H$_2$O
A. How many steps are in the reaction mechanism?
   a. There’s three transition states (or three peaks) so three steps in reaction mechanism

B. Label the Ea and ΔH° for each step and the ΔH° overall for the reaction
C. Draw the structure of the transition state for each step and indicate its location on the energy diagram.
D. Which step is the rate-determining? Why?
   a. Step 2, because it has the highest activation energy, and its transition state is most unstable.

Chapter 13
14. Tell how IR spectroscopy could be used to determine if the reaction is complete. (13.41)

A. a. Look out for the disappearance of C=C peak at 1650 cm⁻¹
B.

a. Check for disappearance of C=C peak at 1650 cm$^{-1}$ and appearance of C=O peak at 1700 cm$^{-1}$

15. Match each compound to its IR spectrum (13.42)
a. Phenyl peaks observed around 1600 to 1500 cm\(^{-1}\) and Csp\(^2\)-H peaks observed at around 3150 cm\(^{-1}\)
a. ES

Alcohol peak observed at 3600 to 3200 cm\(^{-1}\)

**Chapter 14**

16. Into how many peaks will the signal for each of the indicated protons split? (14.44)

A.
a. The green chemically equivalent hydrogens have no neighboring hydrogens, thus it will be a singlet peak. The blue hydrogen has two neighboring hydrogens, thus it will be a triplet peak

B.

a. The green hydrogens have three neighboring hydrogens, thus it will be a quartet peak and the blue hydrogen has two neighboring peak so it is a triplet peak

17. Identify the carbon atoms that give rise to each NMR signal. (14.31)

Carbon $C_b$ is the most deshielded (highest chemical shift) because it is adjacent to an electron withdrawing alcohol group. On the other hand carbon $C_d$ is most shielded (lowest chemical shift) because it is the furthest away from the alcohol group. Based on this observation, we can label the carbon peaks as such. Between carbon $C_c$ and $C_a$, $C_c$ will be more shielded because it is adjacent to electron donating methyl groups.
a. \( \text{CH}_3\text{CH(OH)CH}_2\text{CH}_3 \)

- \( C_a \)
- \( C_{c} \)
- \( C_{b} \)
- \( C_d \)