1. Give the IUPAC name for each compound. (4.44 3rd Edition)

Redraw into skeletal structure form (Remember the 2 extra carbons in the newman projection that are not written out in the condensed form)

4-isopropylheptane  
3-ethyl-3-methylpentane  
4,4-diethyl-5-methyloctane

Find the longest parent chain, number the chain giving the lowest combination of numbers to the substituents, then write out the name in alphabetical order.

2. Consider Newman projections (A-D) for four carbon-carbohydrates. How is each pair of compounds related: (a) A and B; (b) A and C; (c) A and D; (d) C and D? Choose from identical molecules, enantiomers, or diastereomers? (5.60 3rd Edition)

Redraw into skeletal structure form, with stereochemistry. The substituents on the right side of the Newman projections should have the same stereochemistry, and the substituents on the left side should also have the same stereochemistry. The ones on the top and bottom should be in the plane.
Final Review Key

a. A and B are identical (same configuration)
b. A and C are enantiomers (flipped at all stereocenters)
c. A and D are diastereomers (flipped at one stereocenter, but not all)
d. C and D are diastereomers (flipped at one stereocenter, but not all)

Enantiomers have opposite configurations at ALL stereocenters. Diastereomers have at least one stereocenter flipped, but not all of them.

3. For the compound drawn below: (4.49 3rd Edition)

![Compound Diagram]

a. Draw representations for the cis and trans isomers using a hexagon for the six-membered ring, and wedges and dashes for the substituents.

Cis (or both dashed) Trans (or both flipped)

b. Draw the two possible chair conformations for the cis isomer. Which conformation, if either, is more stable?

More stable
The bulkier t-butyl group is more stable when in the equatorial position, as there is less steric strain.
Final Review Key

c. Draw the two possible chair conformations for the trans isomer. Which conformation, if either, is more stable?

![Chair Conformations]

More stable
Both substituents in the equatorial position are more favored because there is less steric strain than with diaxial interactions.

d. Which isomer, cis or trans, is more stable and why?
The trans isomer is more stable because both substituents are in the equatorial position, rather than one in the cis isomer. Again, equatorial positioning is more favored as less steric strain is present, and diaxial interactions are extremely high in energy and unstable.

4. How many degrees of unsaturation are present in each compound? (10.2 3rd Edition)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Degrees US</th>
</tr>
</thead>
<tbody>
<tr>
<td>a. C₂H₂</td>
<td>2</td>
</tr>
<tr>
<td>b. C₇H₈O</td>
<td>4</td>
</tr>
<tr>
<td>c. C₇H₁₁Br</td>
<td>2</td>
</tr>
</tbody>
</table>

When calculating degrees of unsaturation
1. Calculate the maximum number of Hydrogens (2n+2, where n is the number of Carbons)
2. Subtract the actual number of Hydrogens given in the molecular formula from the maximum number
3. Divide by 2
   ● When a Halogen is present, subtract one Hydrogen and when a Nitrogen is present add one Hydrogen (IGNORE Oxygen)

5. Hydrocarbons like benzene are metabolized in the body to arene oxides, which rearrange to form phenols. This is an example of a general process in the body, in which an unwanted compound (benzene) is converted to a more water-soluble derivative, called a metabolite, so that it can be excreted more readily from the body.

![Benzene Transformation]
a. Classify each of the reactions as oxidation, reduction, or neither.
The first conversion adds two C-O bonds, and an increase in C-Z bonds is an Oxidation reaction. The second reaction has the loss of one C-O bond and the loss of one C-H bond so this is neither oxidation or reduction, as two different things are occurring, that contradict each other in terms of defining oxidation and reduction.

b. Explain why phenol is more water soluble than benzene.
Phenol is more water soluble than benzene, as it has an Oxygen, which makes the molecule polar, whereas benzene is nonpolar. This O-H bond is able to Hydrogen bond with water, while benzene cannot, as it has no N-H or O-H bonds.

6. Draw the eight constitutional isomers having the molecular formula C₅H₁₁Cl. Label any stereogenic centers. (5.40 3rd Edition)

[Drawings of eight constitutional isomers]

Calculate degrees of unsaturation, using above method from question 4. Since there are 0 degrees of unsaturation, there should be no double bonds or rings in any of the isomers. Guess and check by moving around substituents, ensuring the same number of Carbons, Hydrogens and Chlorines are present. Then look for Carbons with 4 unique groups. These are stereogenic centers.

7. Draw the structure for each compound. (5.46 3rd Edition)

a. (3R)-3-methylhexane
c. (3R,5S,6R)-5-ethyl-3,6-dimethylnonane

b. (4R,5S)-4,5-diethyloctane
d. (3S,6S)-6-isopropyl-3-methyldecane
When drawing structures from IUPAC names, first draw out the parent chain and add in the substituents on the indicated numbers. Then go through the stereochemistry. The easiest way to do this would be placing hydrogen in the back and seeing what configuration (R or S) each stereocenter has. Then if it doesn’t match the name, put Hydrogen in the front to invert that stereochemistry.

8. Explain each statement by referring to compounds A-E. (5.58 3rd Edition)

a. A has a mirror image, but no enantiomer. Every molecule has a mirror image, but only chiral molecules have enantiomers. A is not chiral, as it has no stereogenic centers, and therefore has no enantiomers.

b. B has an enantiomer and no diastereomer. B has one stereogenic center, which makes it chiral. Therefore it has an enantiomer, but due to the presence of only one stereocenter it cannot have a diastereomer. Compounds must have 2 or more stereogenic centers in order to have diastereomers.

c. C has both an enantiomer and diastereomer. C is both chiral and has two stereogenic centers, so it has both an enantiomer and diastereomer.

d. D has a diastereomer, but no enantiomer. D has two stereogenic centers, but the presence of a mirror plane of symmetry makes this a meso compound, so it is achiral and has no enantiomer.

e. E has a diastereomer, but no enantiomer. E has two stereogenic centers, but the presence of a mirror plane of symmetry makes this a meso compound, so it is achiral and has no enantiomer.
9. Amygdalin, a compound isolated from the pits of apricots, peaches, and wild cherries, is sometimes called laetrile. Although it has no known therapeutic value, amygdalin has been used as an unsanctioned anticancer drug both within and outside of the United States. One hydrolysis product formed from amygdalin is mandelic acid, used in treating common skin problems caused by photo-aging and acne.

a. How many stereogenic centers are present in amygdalin? What is the maximum number of stereoisomers present?

11 stereogenic centers are circled above. Maximum number of stereoisomers: \(2^n\), where \(n = \) number of stereocenters; \(2^{11} = 2048\)

b. Draw both enantiomers of mandelic acid and label each stereogenic center as R or S.

c. Pure (R)-mandelic acid has a specific rotation of -154. If a sample contains 60% of the R isomer and 40% of its enantiomer, what is the \([\alpha]\) of this solution?

\[
\text{ee} = \%R - \%S; 60\% - 40\% = 20\% \text{ ee} \\
\text{ee} = [\alpha]_{\text{soln}}/[\alpha]_{\text{pure}} \times 100; [\alpha]_{\text{soln}} = (\text{ee}/100) \times [\alpha]_{\text{pure}}; [\alpha]_{\text{soln}} = (20/100) \times -154; [\alpha]_{\text{soln}} = -31
\]

d. Calculate the ee of a solution of mandelic acid having \([\alpha]\) = +50. What is the percentage of each enantiomer present?

\[
\text{ee} = [\alpha]_{\text{soln}}/[\alpha]_{\text{pure}} \times 100; (50/154) \times 100 = 32\% \text{ ee} \\
32\% \text{ excess S enantiomer}; 100-32 = 68\% \text{ racemic mixture}; 68/2 = 34\% \text{ of each enantiomer, BUT S has 32\% in excess so } 34 + 32 = 66\% \text{ S and 34\% R}
\]
Final Review Key

10. $E_a$ refers to transition state energy. $\Delta H^\circ$ is the difference between the starting material and products in terms of energy (6.49)
   a. There are three steps. Each hill represents a step.
   b. See below
   c. The rate limiting step is the one with the highest $E_a$ because it requires the most energy.

11. Recall rate rules from general chemistry as well. You will draw the reactants in the equation. Based on that, you are able to calculate what happens when the concentration of those compounds are changed (6.51).
   a. $\text{rate} = k[\text{CH}_3\text{Br}][\text{NaCN}]
   b. \text{Double } [\text{CH}_3\text{Br}] = \text{rate doubles.}
   c. \text{Halve } [\text{NaCN}] = \text{rate halved.}
   d. Increase both $[\text{CH}_3\text{Br}]$ and $[\text{NaCN}]$ by factor of 5 = $[5][5] = \text{rate increases by a factor of 25.}$

12. A general rule of thumbs is that the stronger the bond, the greater the absorption value. (13.37 a/c)
Final Review Key

a.  

\[(\text{CH}_3)_2\text{C}==\text{O} \quad \text{or} \quad (\text{CH}_3)_2\text{CH}==\text{OH}\]

The C=O bond is stronger and, therefore, has a higher absorption value

b.  

\[
\begin{align*}
\text{H} &\quad \text{or} \quad \text{H} \\
\end{align*}
\]

The Double bond with the hydrogen is a stronger bond and, therefore, has the higher absorption.

13. To do these problems, you must be aware of the types of absorption values that exist. Thus, your best method of answering would be to have some values memorized.  (13.38 b, f, e)

  a.  

\[
\begin{align*}
\text{C}_3\text{H}_5 \text{C}==\text{CH} \\
\text{C}_3\text{H}_5\text{C}==\text{CH} &\quad \text{at} \quad 3900 \text{ cm}^{-1} \\
\text{C}_3\text{H}_5\text{C}==\text{CH} &\quad \text{at} \quad 2850-3000 \text{ cm}^{-1} \\
\text{C}_3\text{H}_5\text{C}==\text{CH} &\quad \text{at} \quad 2250 \text{ cm}^{-1} \\
\end{align*}
\]

b.  

\[
\begin{align*}
\text{O} &\quad \text{H} &\quad \text{at} \quad >3000 \text{ cm}^{-1} \\
\text{C}_3\text{H}_5\text{C}==\text{OH} &\quad \text{at} \quad 3000-3150 \text{ cm}^{-1} \\
\text{C}_3\text{H}_5\text{C}==\text{OH} &\quad \text{at} \quad \sim1700 \text{ cm}^{-1} \\
\text{C}_3\text{H}_5\text{C}==\text{OH} &\quad \text{phenyl} \quad \text{group} \quad \text{at} \quad 1600, \quad 1500 \text{ cm}^{-1} \\
\end{align*}
\]

c.  

\[
\begin{align*}
\text{O} &\quad \text{H} &\quad \text{at} \quad 3200-3600 \text{ cm}^{-1} \\
\text{C}_3\text{H}_5\text{C}==\text{OH} &\quad \text{at} \quad 3000-3150 \text{ cm}^{-1} \\
\text{C}_3\text{H}_5\text{C}==\text{OH} &\quad \text{at} \quad 2850-3000 \text{ cm}^{-1} \\
\text{C}_3\text{H}_5\text{C}==\text{OH} &\quad \text{C}==\text{C} \quad \text{at} \quad 1650 \text{ cm}^{-1} \\
\end{align*}
\]
14. To differentiate between two compounds, identify their characteristic bonds/groups. In a, the first group has a C-C triple bond in the middle, whereas the second group has it at the end. Since the first group is symmetric, it does not have an absorption value. For b, there is a characteristic OH (one of the easiest groups to identify on a spectrum), but that there is only an OR group on the left. This, that would be the major difference between them. Lastly, for C, there is a C=O bond in the second molecule, which is also a very common/easily identifiable group on a spectrum. (13.39 e, b, d)

a. 
\[
\text{CH}_3\text{C≡CCH}_3 \quad \text{and} \quad \text{CH}_3\text{CH}_2\text{C≡CH} \\
\text{no C=C absorption} \quad \text{C}_\text{sp}-\text{H bond} \quad 3300 \text{ cm}^{-1} \\
\text{due to symmetry} \quad \text{C=C bond at } \sim 2250 \text{ cm}^{-1}
\]

b. 
\[
\text{CH}_3\text{CH}_2\text{C}-\text{OH} \quad \text{and} \quad \text{CH}_3\text{C}-\text{OCH}_3 \\
\text{O=H bond} \quad \text{no O=H bond} \\
> 3000 \text{ cm}^{-1}
\]

c. 
\[
\text{no C=O bond} \\
\text{C=O bond} \quad \sim 1700 \text{ cm}^{-1}
\]
15. For these types of problems, you must identify the characteristic groups in each molecule and find the associated peaks on the spectrum. Part a has an OH group, b has a C=C double bond (sp2), and c has an aromatic ring. Again, be familiar with these types of peaks as they are very common and can show up on the final exam (13.42 f, b, c).

a. 

Spectrum [2]:

\[(\text{CH}_3\text{CH}_2)_3\text{COH} (F)\]
\[\text{OH at 3600–3200 cm}^{-1}\]

b. 

Spectrum [1]:

\[\text{CH}_2=\text{C(\text{CH}_3)CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 (B)\]
\[\text{C=C peak at 1650 cm}^{-1}\]
\[\text{C}_{sp^2}\text{-H at 3150 cm}^{-1}\]

c. 

Spectrum [4]:

\[\text{CH(CH}_3\text{)}_2 (C)\]
\[\text{C}_{sp^2}\text{-H at 3150 cm}^{-1}\]
\[\text{Phenyl peaks at 1600 and 1500 cm}^{-1}\]

16. Recall that the “kinds of protons” as seen below, simply differ in their environment. They have different surroundings and, thus, are distinct from each other. For example, the protons designated as Ha in question a are next to the same kinds of hydrogens on adjacent carbons- Hb. Hb is next to Hc and Ha. Since this relationship occurs twice, there are multiple Hb protons. Begin by identifying all protons. Then identify the environment of those protons by comparing what atoms/groups are next to them. If two protons are adjacent to the same atoms/groups, they are equivalent (like Hb in example a), but if they are adjacent to different groups, they are considered different protons. (14.35 a/d and 14.36 b)
Final Review Key

a.

3 kinds of protons

b.

4 kinds of protons

c.

vanillin
6 NMR signals
17. When looking for protons that are downfield, look at the more electronegative atom. The more electronegative it is, the more downfield the protons adjacent to it are going to be. Also consider the number of electronegative atoms. The more there are, the more deshielding there is and, therefore, the more downfield the protons will be. (14.39 b / d)

a.

\[
\text{CH}_3\text{CH}_2\text{CH}_2\text{I} \quad \text{or} \quad \text{CH}_3\text{CH}_2\text{CH}_2\text{F}
\]

More electronegative F deshields the H's. farther downfield

b.

\[
\text{CH}_3\text{CH}_2\text{CHBr}_2 \quad \text{or} \quad \text{CH}_3\text{CH}_2\text{CH}_2\text{Br}
\]

Two electronegative Br's deshield the H. farther downfield

18. When it comes to splitting, pick a proton of interest and look at the protons adjacent to it. For example, in problem a, if you choose to focus on Hc, the only adjacent protons are on Hd. Then, count the number of protons in group Hd (3, in this case). Next, add 1 to that number. Doing this, you get 4. This tells you that Hc will be split into 4 parts and will be considered a quartet. Repeat this process for all proton groups. For b, recall that atoms such as oxygen do not split adjacent atoms, so do not consider the H in the hydroxyl group. (14.44 e / f)

a.

\[
\text{(CH}_3\text{)}_2\text{CH} \quad \text{C} \quad \text{OCH}_2\text{CH}_3
\]

H\text{a} protons split by 1 H = doublet
H\text{b} proton split by 6 H's = septet
H\text{c} protons split by 3 H's = quartet
H\text{d} protons split by 2 H's = triplet

b.
19. First calculate the degrees of unsaturation to determine whether a π bond exists. This gives you clues as to whether there is a C=O bond. Next, examine the carbon NMR to identify the number of carbons. In this case, there are 5 peaks, which tells us there are 5 DIFFERENT carbons. Finally, look at the proton NMR. Keep in mind that the further downfield a peak is, the more likely it is next to an electronegative atom (which is chlorine in this case). In the protons NMR, we know that there are 3 CH2 groups and 1 CH3 group. The CH3 group must be in the periphery of the molecule, since a CH3 cannot be in the middle of a molecule. To differentiate between the CH2 groups, we know that 2 of them are downfield. Thus, they must be next to electronegative atoms. As for which one is next to O and which is next to Cl, that depends on electronegativity. Since Cl is more electronegative, the CH2 group next to it will be more downfield. Thus, there must be a ClCH2 group, followed by a regular CH2 group. This leaves an OCH2. Now, based on these values, you can deduce the structure. (14.65)
Final Review Key

20. Begin determining the degrees of unsaturation. In this case, there is 1, which tells you that 1 double bond exists. Given that there is an oxygen atom, it is likely that the bond is between C and O. That can be confirmed by looking at the IR, which has a peak at 1700 cm\(^{-1}\). Next, consider the proton NMR. We know there is a CH group, CH₃ groups and a (CH₃)₂ group. For the last group, we know that is the case because you can not have CH₆. In this case, the only electronegative atom is oxygen, so the proton groups closer to it will be slightly more downfield. However to differentiate which is which, you will need to identify the splitting patterns. The CH₃ group has 1 peak, which tells us it is not next to other protons. Thus, it must be attached to the C=O bond. Next, the CH group has 7 peaks, which tells us it is next to 6 hydrogens. And the (CH₃)₂ group has 2 splits, suggesting it is next to one hydrogen. Thus, the CH and (CH₃)₂ groups must be next to each other and the CH₃ group must be separate. Using these clues, you can deduce the structure below. Note that you can also do this by following the reaction conditions, which have to do with acid base chemistry as well as nucleophilic substitution.

<table>
<thead>
<tr>
<th>Compound Q: Molecular ion at 86.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular formula: C₅H₁₀O:</td>
</tr>
<tr>
<td>1 degree of unsaturation</td>
</tr>
<tr>
<td>IR absorption at ~1700 cm(^{-1}): C=O</td>
</tr>
<tr>
<td>NMR data:</td>
</tr>
<tr>
<td>Hₐ: doublet at 1.1 ppm, 2 CH₃ groups split by 1 H</td>
</tr>
<tr>
<td>Hₖ: singlet at 2.1 ppm, CH₃ group</td>
</tr>
<tr>
<td>Hₜ: septet at 2.6 ppm, 1 H split by 6 H's</td>
</tr>
</tbody>
</table>

Important Concepts from Chapters 4/5/6/Spec:
- Review week 2/3 worksheets for material on chapters 1-3
- Drawing newman projections/Converting newman projections to skeletal form
- Drawing chair conformations/converting to flat rings
- R and S configuration (rotating molecules when H is not in the back)
- Drawing all possible stereoisomers for a given compound
- Chiral, achiral, and meso compounds
- Difference between conformers, enantiomers, diastereomers, and constitutional isomers
- Cis and trans isomers
- Racemic mixtures, enantiomeric excess, specific rotation (know the equations)
- L and D compounds (plane polarized light)
- Classifying substitution, elimination, and addition reactions
Final Review Key

- Drawing curved arrows
- Heterolytic and homolytic cleavage
- Two electron arrows, one electron arrows
- Cation, anion, and radicals
- Enthalpy of reaction
- Keq
- Gibbs free energy
- Endothermic and exothermic reactions
- A-values
- Kinetics of reaction
- Transition states
- Energy diagrams
- Infrared spectroscopy: be familiar with general frequencies for functional groups
- Understanding when protons are equivalent (substitution test)
- NMR spectroscopy: be familiar with chemical shifts, splitting, and integration for proton NMR
- Homotopic vs enantiotopic vs diastereotopic in proton NMR