1. (11.5 pts)

a) Identify each molecule drawn below with the appropriate stereochemical designation. Circle your answer.

b) Circle the correct name for each molecule drawn below.

2. (6 pts)

a) Doxorubicin is useful in the treatment of a variety of cancers including leukemia. Unfortunately it is in limited supply. The structure of doxorubicin and two of its isomers are drawn below. Identify the configuration (R or S) for each chirality center. What is the stereochemical relationship between doxorubicin and II? What is the stereochemical relationship between the doxorubicin and III?

b) The two hydrogens indicated in dextroamphetamine (a potent central nervous system stimulant used to treat ADHD and narcolepsy) are said to be diastereotopic since they are on a carbon next to a chirality center and their replacement by something larger than \(^1\text{H}\) produces diastereoisomers (1S,2S and 1R,2S). If the product (to the right of the arrow) is 1S,2S-configuration, that product was formed from replacing the pro-S hydrogen with deuterium, and likewise replacement of the pro-R hydrogen in the starting material by deuterium gives the 1R,2S-configuration. Correctly identify the two hydrogens in the starting material as pro-R or pro-S.
3. (11.5 pts)

a) For the 1,2,4-trifluorocyclohexane molecule that is drawn below, show the conformation that is formed after a chair-chair interconversion. You must use the framework as it is numbered on the right in giving your answer. Additionally, calculate the energy difference between the two conformers (use 0.4 kJ/mol for any of the gauche interactions involving fluorine). Show your calculation.

\[ \Delta G = 0.86 \text{ kJ/mol} \]

b) Draw the structure of the dehydrohalogenation product (III) that will be formed in the following E-2 reaction. Only one of the two starting materials (I, II) will produce this product. Which stereoisomer, I or II, produces the dehydrohalogenation product (III). Explain.

c) Use the framework provided to draw the Newman projection for the starting material in the E-2 reaction shown below. Make it easy on yourself and draw the Newman projection that will allow you to select the identity of the product that will form. Which product is formed?

d) Methyl formate \([\text{C}_2\text{H}_4\text{O}_2]\) reacts (using a lone-pair) with a proton to give the ion, \([\text{C}_2\text{H}_4\text{O}_2]^+\). Draw this ion’s structure and show a reasonable resonance structure for it. Be careful.
5. (18 pts)

a) The equation drawn below shows the possible products that can be formed in the free-radical halogenation of cyclopentene. Assign the statistics to each product that can form. If you wanted a relatively higher concentration of product II (substituted with either bromine or chlorine) would it be better to perform bromination or chlorination? Explain fully.

\[
\text{cyclopentene} + \text{Br}_2 (\text{Cl}_2) \rightarrow \text{Br-cyclopentene} + \text{Br-cyclopentene} + \text{H-Br (H-Cl)}
\]

statistics: I = 2; II = 4; III = 2

b) The last step in the hydration mechanism to produce 1-ethylcyclohexan-1-ol is given below. Only one of the two (I, II) reaction coordinates is correct for this step. Which one is it, I or II? Using Hammond’s postulate, identify which transition state (TS\textsubscript{a} or TS\textsubscript{b}) is appropriate for that step. Explain.

\[
\text{A} \quad \text{TS} \quad \text{B}
\]

\[
\text{A} \quad \text{TS} \quad \text{B}
\]

c) A primary isotope effect (k_D/k_H = 7) is observed for the dehydrohalogenation reaction shown below. Does this reaction follow the E-2 or E-1 mechanistic pathway? Carefully explain your choice.

\[
\text{Ph} + \text{O} : \text{Li} \rightarrow \text{LiCl} + \text{Ph} + \text{H} : \text{O} ^{-} \quad \text{E-2}
\]

H is removed in the RDS so k_D/k_H > 1.

d) Outline the mechanism for the following dehydration reaction (E-1). Show the motion of all electron movement with arrows, and supply the structures of the intermediates in the boxes.

\[
\text{Ph} \quad \text{H} : \text{O} ^{-} \quad \text{Ph} \quad \text{Ph} \quad \text{H}_2\text{O} \quad \text{Ph} \quad \text{Ph} \quad \text{H} _2\text{O} ^{+}
\]
6. (9 pts)

a) Which product, a or b, will be formed in the following S_N2 reaction? Explain. Products A and B are formed by attack at positions a and b respectively.

b) What reagents and solvents would be required to carry out the following transformations (major organic products are shown)? What is the stereochemical relationship between I and II?

c) Which intermediate product, A or B, will be formed when ethanol opens the bromonium ion? Explain. The intermediates, A and B, are formed from attack by ethanol at positions a and b respectively.

7. (22 pts)

a) As part of your preparation for 217 you should begin thinking about combinations (synthesis) of reactions you have learned, in order to build molecules of greater complexity. The chemical conversion shown below requires 3 steps. Which order of steps is correct?

b) Identify the structures of the products formed in the following reactions.

Grubb's

(Cy3P)2Cl2Ru=CHPh

H2/Pd

H2

c) Identify the structure of the major products that are formed in each of the following reactions and indicate the stereochemistry where it is important. For reactions where a mixture of enantiomers can form, showing a single enantiomer is permissible.

HBr

Hg(OAc)2 / H2O

OsO4/H2O2

NaBH4
d) When α-pinene (2,6,6-trimethylbicyclo-[3.1.1]-hept-2-ene) undergoes hydrogenation with deuterium, $^2$H$_2$, a single isomer is formed. Given that result, which principle product will form, exo- or endo-, when the epoxide is prepared by reaction with the peroxycacid, mCPBA?

![Diagram of α-pinene and epoxide formation]

8. (10 pts)

a) A molecule of formula C$_6$H$_{10}$O$_2$ has significant peaks that appear in the infrared spectrum at 1722 and 1782 cm$^{-1}$. There are six lines in the CNMR as shown below. In the DEPT-135 the peaks at 167.5 and 136.78 disappear, and in the DEPT-90 all of peaks disappear. In the DEPT-135 the peaks at 125.1 and 60.78 are inverted while the peaks at 18.3 and 14.38 are positive. Determine the structure for this molecule. Show your work.

![CNMR spectrum showing six lines]

b) The CNMR spectrum (9 lines) for a molecule of formula C$_6$H$_{14}$O$_2$ is shown below. In the IR spectrum there are significant peaks at 2850, 2700, 1685, 1625, 1260 and 825 cm$^{-1}$. Determine the structure of this material. Show all of your work including calculation of the units of unsaturation for full or partial credit, and assign significant peaks to their characteristic structural features in the spectrum.

![CNMR spectrum showing nine lines]