Solve the following problems in the space provided. You have up to 120 minutes to complete this closed book, closed notes exam. Please take the exam in a quiet, controlled area such as a classroom. When you are in doubt, rely on your logic rather than vague memories. Budget your time according to the point value of the problem. It is better to do most of an exam well than all of it poorly.

My office no. 610-526-5102, My home no. 610-254-9619, My cell is 610-888-4530
My email address mnerzsto@brynmawr.edu. I can’t guarantee I can answer all questions, but texting is probably the best way to get me quickly.

1. Write all the stereoisomers for the following structure. Assign absolute configuration to all assignable stereocenters (R/S). Establish relationships between the molecules and identify any meso compounds. Identify one molecule, if isolated, that would give an optical rotation. (20 points)
2. Decide whether or not the following pairs of molecules can be distinguished based on the given physical or chemical property. You will receive partial credit for establishing the relationship between molecules. (20 points)

a. reaction with an optically pure chiral base  
   b. solubility in sodium hydroxide solution
   
   ![Enantiomers](image)

   Enantiomers
   * rxn w chiral will give
   * diastereomers which should be separable

   ![Diastereomers](image)

   diastereomers
   * Both ca. acids
   * Both will react
   * In principle salts can be differentiated

b. proton nmr spectroscopy  
   d. optical rotation

   ![Structural Isomers](image)

   Structural Isomers
   * 4 different aromatic hydrogens
   * 2 different aromatic hydrogens

   ![Structural Isomers](image)

   Structural Isomers
   * One is meso one is chiral

   ![Structural Isomers](image)

   Structural Isomers
   * Meso has 0 rotation
   * Chiral has rotation

   ![Structural Isomers](image)

   Structural Isomers
   * One is meso one is chiral

   ![Structural Isomers](image)

   Structural Isomers
   * Meso has 0 rotation
   * Chiral has rotation
3. An unknown compound having the formula $C_{10}H_{12}O_2$ is studied by $^1H$ NMR and the spectrum is given below. Fully interpret the given information and propose the structure of the unknown compound. Generous partial credit will be given for structural fragments. (18 points)
4. Write in the reagents needed to carry out the following transformations. The product does not have to be the exclusive product, but should be a reasonable product from the reactions you have studied. (15 points)

a.

\[ \text{CH}_3\text{OH}, \text{THF} \]

b.

\[ \text{H}_2, \text{Pd} \]

c.

\[ \cdot\text{Cl}_2 \]
5. Write the alkene (specify stereochemistry of the alkene) and the reagents needed to make the following molecules. Note the synthesis should be one step. (16 points)

a.

b.
7. Consider the following molecule.

Using Newman projections, draw all the relevant conformers for the above molecule. For each conformer, label all stabilizing and destabilizing interactions. Establish the highest energy conformer or conformers and establish the lowest energy conformer or conformers. (16 points)

What is torsional angle between the hydrogens in the molecule? How would this torsional angle be manifested in the proton NMR? (8 points)
8. Carry out a complete conformational analysis of 1S, 2S, 4R 1-bromo-4-(methylethyl)-2-methylcyclohexane. Given the information that a 1,3 diaxial interaction between a (methylethyl) and a hydrogen is 4.6 kJoule/mole and the same interactions between a bromine and a hydrogen and a methyl and a hydrogen are 1.0 kJoule/mole and 3.76 kJoule/mole, respectively, calculate the energy difference between the two conformers and ascertain which conformer is more abundant in the population. (28 points)

\[
\begin{align*}
\text{Br} & \quad \text{H} \\
2 \text{ BrCH} & \quad 2 \text{ H} \\
3.76 \times 76 & = 284.88 \text{ kJ/mol}
\end{align*}
\]

9. Consider the following molecules in solution in equimolar proportions. Would the solution be optically active (rotate plane polarized light)? Partial credit will be given for ascertaining the chirality of the individual molecules in the mixture. (16 points)

Net rotation: Meso achiral chiral

Identify the pair of enantiomers in the above group of molecules. Explain how that pair might be separated in a conceptual way. It is best to outline this process using structures. Once again this is not an essay question. (10 points)

\[R + S \rightarrow R-S^* \text{, remove S} \rightarrow R+S^* \text{, diastereomers separable}\]
10. Compound X has the formula C$_8$H$_{14}$O$_3$. When the IR spectrum of X is measured, two strong absorptions are observed around 1715 cm$^{-1}$. The H NMR spectrum of X is given below. Write a structure that is consistent with this information. Show all work to ensure maximum partial credit. (20 points)
12. Write complete mechanisms for the following reactions. This requires that you use the arrow formalism and show the stereochemistry of products where appropriate. Also show resonance hybrids where appropriate.

(40 points)

a.

b.
c. 

\[
\text{HBr} \quad \xrightarrow{\text{CH}_3\text{COOOCOCH}_3} \quad \text{light or heat}
\]

\[
\text{R}^-\text{O}^-\text{O}^-\text{R} \quad \rightarrow \quad 2\text{RO}^-
\]

\[
\text{R}^-\text{O}^-\text{H} + \text{Br}^- \quad \rightarrow \quad \text{R}^-\text{O}^-\text{H} + \text{Br}^-
\]

d. 

\[
\text{Li}^-\text{H} + \xrightarrow{\text{Li}} \quad \text{anion on ring}
\]

No resonance effect but moderate polar effect.

(3) is vinylic and gives sp^2 anion on C.
12. Consider the circled protons in the following molecule and rank them with regard to acidity. Justify your order, using acid base theory and resonance theory if necessary. (16 points)

Resonance stabilized anion
weak base, \( \overset{\circ}{\circ} \) conegate

\( 2 \) is effect and gives \( sp^2 \)
anion on nitrogen
No resonance effect
but moderate polar effect

\( 3 \) is vinylic and gives \( sp^2 \)
anion on C