1. (8 pts) Draw or name the following compounds using IUPAC nomenclature as appropriate.

\[(\text{R})-4\text{-bromo-6-methyl-1-heptene} \]
\[
\text{or } (\text{R})-4\text{-bromo-6-methylhept-1-ene}
\]

\[
\text{give alkene lowest } \# \]

\[(\text{R})-1\text{-phenyl-1-propanol or (R)-1-phenylpropan-1-ol} \]

4-(2-chloroethyl)-3-methyldecane

1. (8 pts) From the molecules below identify a pair of enantiomers, a pair of diastereomers, and a meso compound. Be sure to write your answers in the provided boxes.

Enantiomers: \( \text{A} \) & \( \text{E} \)

or \( \text{F} \) & \( \text{E} \)

Diastereomers: \( \text{B} \) & \( \text{A} \) or \( \text{F} \)

or \( \text{B} \) & \( \text{C} \) or \( \text{E} \)

Meso: \( \text{B} \)

Note: \( \text{A} \) & \( \text{F} \) are the same compound

\( \text{C} \) & \( \text{E} \) are the same compound
1. (3 pts) Suppose a sample of an optically active substance has an observed rotation of +20°. The scale on the analyzer of the polarimeter is circular; that is, +20° is the same as –340°, or +380° etc. How would you determine whether the observed rotation is +20° or some other value?

Since optical rotation is dependent on concentration and path length, the simplest solution would be to dilute the sample in half. Therefore, if the rotation were truly +20° then the new rotation at half concentration would be +10°; if –340° then –170°; if +380° then +190°, etc.

1. (12 pts) Provide the structure of the major organic product or products expected from each of the following reactions. Write "NR" if no reaction. Indicate stereochemistry where applicable.

- \( \text{Br} \) \( \text{E2} \)
- \( \text{ONa} \) \( \text{E2 w/ bulky base!} \)
- \( \text{H}_2\text{N} \) \( \text{Br} \) \( \text{DMSO} \) \( \text{intramolecular} \)
- \( \text{CH}_3\text{OH} \) \( \text{(ignore elimination pdts)} \) \( \text{S}_{\text{N}1} \) \( \text{w/ rmgmnt} \)
- \( \text{ONa} \) \( \text{E2} \)
- \( \text{NaCN} \) \( \text{DMF} \) \( \text{S}_{\text{N}2}: \text{inversion} \)
2. (3 pts) Mesylate and tosylate are nearly equivalent in their ability to act as leaving groups. The triflate group, however, is many times better than either of these. Explain this observation.

The strongly electronegative trifluoromethyl group (3 F’s!) greatly enhances the triflate’s ability as a L.G. The resulting negative charge (after it has left) is stabilized by the inductive effect of the –CF₃ group. As you might suspect, trifluorosulfonic acid (the conjugate acid) is a strong acid.

3. (5 pts) Below are the relative rates of solvolysis in methanol for compounds A, B, and C. Explain this observation.

\[
\text{PhCH}_2\text{Br} \quad < \quad \text{Ph}_2\text{CHBr} \quad < \quad \text{Ph}_3\text{CBr} \\
\text{A} \quad \text{B} \quad \text{C}
\]

As methanol is a weak nucleophile, each of these substrates will react via an S₉₁ process. Consider the stability of the intermediate carbocations for halides A, B, and C: Compound A will generate the least stable carbocation and C the most stable. Therefore, the hard step (the rate-determining step) will be more easily accomplished (= faster) in the order shown above.

4. (7 pts) (S)-(+-)MDMA, also known as ‘X,’ has been identified as the more potent stereoisomer in inducing serotonin release from rat brain synaptosomes. MDMA has receptor binding affinities for various brain recognition sites. Research has shown that some select binding sites are irreversibly damaged in both rat and human subjects.

a) Draw the more potent stereoisomer of MDMA.
b) When (S)-(+-)MDMA is allowed to react with benzyl bromide (PhCH₂Br) two different products are obtained that can be easily separated. It is found that these products have different m.p. and [€]D values and different NMR spectra. Draw both of these compounds.
c) What is the relationship between the two compounds in part (b)? They are diastereomers.
5. (15 pts) For each pair of reactions below, predict which proceeds the fastest, by what mechanism (e.g., S_N1, S_N2, E1, or E2), and briefly explain why.

a) \[ \text{Cl} \rightarrow \text{SH} \]
   \[ \text{I} \rightarrow \text{SH} \]
   L.G. ability: I > Br > Cl
   \( S_N2 \)

b) \[ \text{Cl} + \text{H}_2\text{O} \rightarrow \text{OH} \]
   A more stable carbocation will result:
   \[ \overset{+}{\text{CH}} \] > \[ \overset{+}{\text{CH}} \]
   \( 2^\prime, \text{allylic} \)
   \( S_N1 \)

c) \[ \text{I} \rightarrow \text{OH} \]
   \[ \text{I} \rightarrow \text{OH} \]
   Ag⁺ will accelerate the reaction by coordinating to the Br, thereby enhancing the electrophilicity of the \(-\)C
   \( S_N2 \)

d) \[ \text{Cl} \rightarrow \text{P(CH}_3)_3 \]
   \[ \text{Cl} \rightarrow \text{P(CH}_3)_3 \]
   less \(-\)branching
   \( S_N2 \)

e) \[ \text{Br} \rightarrow \text{C} \]
   \[ \text{Br} \rightarrow \text{C} \]
   significant ring strain will develop in the top case as the \(-\)C goes from \( sp^3 \) to \( sp^2 \) (109.5° to 120°)
   \( E2 \)
6. (16 pts) Clearly circle the correct answer for the following questions. There is only one correct answer for each; no credit will be given if more than one answer is circled for each question.

a) Which of the following alkyl halides can produce more than one product in an E2 reaction?

b) Which of the following is an H-bond donor?

c) A molecule with two stereocenters and one meso form will have how many stereoisomers?

- four
- three
- two
- one

d) Identify the strongest base from among the following:

- ONa
- O
- O
- O

- ONa

- OH

e) Which of the following Fischer projections represents (R)-2-methoxybutane?

f) What is the optical rotation for (S)-4-chlorodecane?

- dextrorotatory
- levorotatory
- cannot tell

g) Select from among the following the best solvent for an S_N2 reaction.

- H
- CH_3
- O
- = DMF

h) What percent of (R)-3-hexanol is present in a solution that has 30% ee of the (S) enantiomer?

- 65%
- 30%
- 35%
- 70%
7. (8 pts) Provide a complete and detailed mechanism for the following reaction. Be sure to clearly show arrows, lone pairs, and formal charges.

\[
\begin{align*}
\text{Br}^{-} + \text{C}_5\text{H}_9\text{Br} &\xrightarrow{\text{CH}_3\text{OH}} \text{C}_5\text{H}_9\text{H} \\
\text{C}_5\text{H}_9\text{H} &\xrightarrow{\text{CH}_3\text{OH}} \text{C}_5\text{H}_9\text{OCH}_3 + \text{CH}_3\text{OH}_2
\end{align*}
\]

*2° carbocation*  
*2°, allylic carbocation*

8. (5 pts) Complete the following reaction-coordinate diagram for the reaction in the preceding question. Label any intermediates (I) and transition states (≠) encountered. (You do not need to label \(E_a\), \[\Delta H\], etc.)
9. (6 pts) Two isomeric $\text{S}_2\text{N}_2$ products are possible when sodium thiosulfate is exposed to iodomethane.

a) Provide the structures of these two products.
b) Only one of these products is formed. Which one is formed and why?

Product 1: 
\[
\text{CH}_3\text{S}-\text{O}\quad \text{Na}
\]

Product 2: 
\[
\text{Na} \quad \text{S}-\text{O}-\text{CH}_3
\]

Sodium thiosulfate is an ambident nucleophile. Either the negatively charged S or O can attack iodomethane. As S is more polarizable, it is the better nucleophile and therefore the first product is formed exclusively.

10. (4 pts) Provide reasonable resonance structures for each of the following. Be sure to clearly show all lone pair electrons and formal charges.