1. Rank the following compounds in the trend requested. (15 points each)

a. Rank by stability. The most stable anion is 1, while the least stable anion is 5.

b. Rank by reaction rate in a bromination reaction. The compound that reacts the fastest when photolyzed with bromine is 1, while the compound that reacts the slowest is 5.

c. Rank the following compounds by $S_N1$ reactivity. The compound that would react the fastest in a $S_N1$ reaction is 1, while the compound that would react the slowest is 5.
2. Answer the following halogenation questions.

a. (10) How many constitutional isomers are obtained when each of the following compounds undergoes monochlorination? Write the appropriate number next to each compound.

b. (8) Draw the product(s) obtained when 3,3,6-trimethylcyclohexene undergoes monobromination.

c. (6) There are three constitutional isomers with molecular formula C₅H₁₂. Chlorination of one of these isomers yields only one product. Identify the isomer and draw the product of chlorination.

The four methyl groups are related by symmetry, therefore only one product would be obtained.

d. (6) Of the three constitutional isomers in part c, which isomer reacts with the fastest rate in a bromination reaction? Identify the isomer and draw the product of bromination.

Only isomer that would generate the more stable 3° radical.
3. Consider the structure of the following solvents when answering the questions. Must explain your answer for each question.

![Chemical Structures]

a. How would the rate of this reaction change if the solvent was changed from methanol to DMF?

\[
\text{Br} \quad \text{NaSH} \quad \text{NH}_3
\]

This is a S$_\text{N}$2 reaction between the nucleophilic sodium sulfide and the 1° alkyl halide. The aprotic DMF solvent will allow a faster rate as the nucleophile will have less hydrogen bonding with solvent.

Rate would increase.

b. How would the rate of this reaction change if the solvent was changed from methanol to hexanes?

\[
\text{Br} \quad \text{NaN}_3
\]

This is a unimolecular reaction, probably S$_\text{N}$1, using the 3° alkyl halide. As the solvent decreases in polarity going to the hexanes solvent, the rate would decrease as the charged transition state will not be as stabilized.

Rate would decrease.

c. How would the rate of this reaction change if the solvent was changed from hexanes to DMSO?

\[
\text{Cl} \quad \text{NH}_2 \quad \Delta
\]

This is an intramolecular S$_\text{N}$2 reaction. The starting material is uncharged, while the transition state would develop partial positive charge on nitrogen and partial negative charge on chloride leaving group. Going to a more polar DMSO solvent will stabilize the transition state more and increase the rate.

Rate would increase.
4. Indicate the preferred product for the following reactions. Only draw the product obtained in highest yield. Multiple answers will be counted wrong. (7 points each)

a. 

\[
\begin{align*}
\text{H}_3\text{C} & \quad \text{Br} \\
\text{H} & \quad \text{H} \\
\text{CH}_3 & \\
\end{align*}
\]  
\[\text{CH}_3\text{SNa} \rightarrow \]
\[
\begin{align*}
\text{H}_3\text{C} & \quad \text{CH}_3 \\
\text{H} & \quad \text{SCH}_3 \\
\end{align*}
\]

b. 

\[
\begin{align*}
\text{CH}_3 \quad \text{C} & \quad \text{H}_3 \quad \text{Br} \\
\text{H} & \quad \text{H} \\
\text{CH}_3 & \\
\end{align*}
\]  
\[\text{CH}_3\text{SNa} \rightarrow \]
\[
\begin{align*}
\end{align*}
\]

c. 

\[
\begin{align*}
\text{Br} & \\
\end{align*}
\]  
\[\text{CH}_3\text{OH} \rightarrow \]
\[
\begin{align*}
\text{OCH}_3 & \\
\end{align*}
\]

d. 

\[
\begin{align*}
\end{align*}
\]  
\[\text{Br}_2, \text{hv} \rightarrow \]
\[
\begin{align*}
\text{Br} & \\
\end{align*}
\]

e. 

\[
\begin{align*}
\text{Br} & \\
\end{align*}
\]  
\[\text{CH}_3\text{OH} \rightarrow \]
\[
\begin{align*}
\text{OCH}_3 & \\
\end{align*}
\]

f. 

\[
\begin{align*}
\text{H} & \quad \text{N} \quad \text{C} \quad \text{H}_3 \quad \text{Br} \\
\end{align*}
\]  
\[\text{CH}_3\text{OH} \rightarrow \]
\[
\begin{align*}
\text{N} & \\
\end{align*}
\]

g. 

\[
\begin{align*}
\text{Br} & \\
\end{align*}
\]  
\[\Delta \rightarrow \]
\[
\begin{align*}
\text{Br} & \\
\text{N} & \\
\end{align*}
\]

h. 

\[
\begin{align*}
\text{H} \quad \text{O} \quad \text{C} \quad \text{H}_3 \quad \text{Br} \\
\text{H} & \quad \text{O} \\
\end{align*}
\]  
\[\text{CH}_3\text{ONa} \rightarrow \]
\[
\begin{align*}
\text{H} & \\
\text{O} & \\
\end{align*}
\]

i. 

\[
\begin{align*}
\text{Br} & \\
\end{align*}
\]  
\[\text{Br} \rightarrow \]
\[
\begin{align*}
\text{S} & \\
\end{align*}
\]
5. Indicate how to synthesize the product shown using the starting material indicated. You can use any other reagents you desire, but you must use the starting material indicated. More than one step may be required. (12 points each)

a. Need to add a leaving group through bromination and then have an S$_{N}$2 reaction.

b. Due to stereochemistry, will need to run two successive S$_{N}$2 reactions.
6. Predicting whether a reaction undergoes a $S_{N}2$, $S_{N}1$, E2, or E1 mechanism is most difficult when a secondary alkyl halide is used. Consider what will occur if the following alkyl halide is used:

\[
\begin{array}{c}
\text{Br} \\
\end{array}
\]

a. (14) If the compound shown reacts with sodium methoxide, either a substitution or elimination product may be obtained. Draw the structure of the substitution and elimination product obtained if the alkyl halide shown is reacted with sodium methoxide.

\[
\begin{array}{c}
\text{OCH}_3 \\
\end{array}
\quad
\begin{array}{c}
\text{H}_3\text{C} \\
\end{array}
\]

Substitution product

Elimination product

b. (6) Draw the structure of the transition state that yields the elimination product when the alkyl halide shown is reacted with sodium methoxide.

\[
\begin{array}{c}
\text{Br} \\
\end{array}
\]

\[
\begin{array}{c}
\text{H} \\
\text{OCH}_3 \\
\end{array}
\]

c. (14) If the alkyl halide shown is heated with methanol, either a substitution or elimination product may be obtained. Draw the structure of the substitution and elimination product obtained if the alkyl halide shown is heated with methanol.

\[
\begin{array}{c}
\text{H}_3\text{CO} \\
\end{array}
\quad
\begin{array}{c}
\text{H}_3\text{C} \\
\end{array}
\]

Substitution product

Elimination product

d. (6) Draw the preferred product if the alkyl halide shown is reacted with sodium cyanide (NaCN).

\[
\begin{array}{c}
\text{CN} \\
\end{array}
\]

e. (6) If the alkyl halide used in parts a-d was modified to the structure shown below, what would be the preferred product if reacted with sodium methoxide?