1. (36 pts) Complete the equations for the following reactions. Show all organic products – if two or more alkene products form, indicate the major product. Indicate proper stereochemistry where necessary.
   a. 
   \[
   \text{ClCH}_2\text{CH}_2\text{Cl} + \text{NaI} + \text{HOCH}_2\text{CH}_3 \rightarrow \\
   \]
   b. 
   \[
   \text{ClC}_6\text{H}_4 + \text{NaSH} + \text{DMSO} \rightarrow \\
   \]
   c. 
   \[
   \text{BrC}_6\text{H}_4 + \text{DBU} + \text{DMSO} \rightarrow \\
   \]
   d. 
   \[
   \text{HC} = \text{CHCl} + \text{NaCN} \rightarrow \\
   \]
   e. 
   \[
   \text{HC} = \text{CHCl} + \text{HOH, } \rightarrow \\
   \]
   f. 
   \[
   \text{CH}_3\text{CH}_2\text{Cl} + \text{KO} + \text{DMF} \rightarrow \\
   \]
   g. 
   \[
   \text{C}_6\text{H}_5\text{Br} + \text{CH}_3\text{CN} \rightarrow \\
   \]
   h. 
   \[
   \text{CH}_2\text{CH}_2\text{H}_2\text{I} + \text{HMPA} \rightarrow \\
   \]
   i. 
   \[
   \text{C}_6\text{H}_5\text{Br} + \text{HOCH}_3 \rightarrow \\
   \]

2. (6 pts) Name compounds a. and b.; draw the structure of compound c.:
   a. 
   \[
   \]
   b. 
   \[
   \]
   c. 
   \[
   \text{trans-1-chloro-3-iodocyclobutane} 
   \]
3. (6 pts) Place the appropriate solvent (DMSO or HOCH₃) under the reaction arrow for each of the following substitution reactions so that they proceed in the forward direction. Explain your choice at the right.

\[
\begin{align*}
\text{Cl} & \quad \text{Nal} \quad \text{Solvent?} \quad \longrightarrow \quad \text{I} \\
\text{I} & \quad \text{NaCl} \quad \text{Solvent?} \quad \longrightarrow \quad \text{Cl}
\end{align*}
\]

4. (21 pts) Consider the following E2 reaction:

\[
\text{Br} + \quad \text{O} \quad \longrightarrow \quad \text{H} + \quad \text{Br} + \quad \text{HO}
\]

a. What is the rate equation for this reaction?

b. Using proper Lewis structures and curved arrow formalism, propose a mechanism for this process.

c. Draw an energy diagram. Label the axes, starting material, product, \( E_A \) and \( \Delta H_{rxn} \); Draw the structures of the transition states for the rate limiting step and any reactive intermediates; identify the rate limiting step.

5. (4 pts) Predict which of the following substrates would undergo E1 more rapidly. Explain your choice.

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

6. (4 pts) The following S_N2 reaction yields a product with the given empirical formula. Suggest a structure for this compound and briefly show how it formed:

\[
\begin{align*}
\text{OH} & \quad \text{Br} \quad \text{KOH} \quad \longrightarrow \quad \text{C}_6\text{H}_{12}\text{O}
\end{align*}
\]
7. (8 pts) Each of the following alkyl bromides gives only one product in E2 elimination. What is the stereochemical relationship between the two products?

\[
\text{Br} \quad \text{E2} \quad \text{Br}
\]

8. (5 pts) Cyclopropyl bromide reacts \(10^4\) times slower than isopropyl bromide in an S\(_\text{N}2\) reaction in a polar aprotic solvent with any given nucleophile even though both are 2° alkyl halides. Suggest a reason for this. Possible considerations would be the mechanism, transition state, kinetics, thermodynamics or other concepts we covered in class.

\[
\begin{align*}
\text{isopropyl bromide} & & \quad \text{cyclopropyl bromide} \\
& & \\
\text{Br} & & \quad \text{Br}
\end{align*}
\]

9. (5 pts) The S\(_\text{N}1/S\(_\text{N}2/E1/E2\) reactions you have learned are very important for the understanding of biochemistry. One step in the urea cycle for ridding an organism of ammonia is the conversion of arginosuccinate to the amino acid arginine plus fumarate.

a. What reaction is occurring here? _____

b. On the structure below show the arrow formalism for the mechanism.

c. Draw the structure of the arginine leaving group in the space provided.

\[
\text{Arginine} + \text{H-Base}
\]

10. (5 pts) In class we used the model of hyperconjugation to explain relative carbocation stabilities. How does the data below for the relative rates of S\(_\text{N}1\) reaction for the illustrated substrate support the hypothesis?

<table>
<thead>
<tr>
<th>R</th>
<th>Relative Rate*</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH(_3)-</td>
<td>540</td>
</tr>
<tr>
<td>CH(_3)CH(_2)-</td>
<td>125</td>
</tr>
<tr>
<td>(CH(_3))(_2)CH-</td>
<td>27</td>
</tr>
<tr>
<td>(CH(_3))(_3)C-</td>
<td>1</td>
</tr>
</tbody>
</table>

*Relative rate means (for example) that the reaction for \(R = CH_3\) is 540 times faster than the reaction for \(R = (CH_3)_3C^-\)

Score _____/100  Approx. Course Grade: _____
1. (36 pts) Complete the equations for the following reactions. Show all organic products – if two or more alkene products form, indicate the major product. Indicate proper stereochemistry where necessary.

   a. \[
   \begin{array}{c}
   \text{Cl} \\
   \text{Cl}
   \end{array}
   \xrightarrow{\text{Nal, HOCH}_2\text{CH}_3}
   \begin{array}{c}
   \text{I} \\
   \text{I}
   \end{array}
   \]

   b. \[
   \begin{array}{c}
   \text{Cl}
   \end{array}
   \xrightarrow{\text{NaSH, DMSO}}
   \begin{array}{c}
   \text{SH}
   \end{array}
   \]

   c. \[
   \begin{array}{c}
   \text{Br}
   \end{array}
   \xrightarrow{\text{DBU, DMSO}}
   \begin{array}{c}
   \text{H}
   \end{array}
   \]

   d. \[
   \begin{array}{c}
   \text{I}
   \end{array}
   \xrightarrow{\text{NaCN}}
   \begin{array}{c}
   \text{CN}
   \end{array}
   \]

   e. \[
   \begin{array}{c}
   \text{I}
   \end{array}
   \xrightarrow{\text{HOH, } \beta}
   \begin{array}{c}
   \text{OH} \\
   \text{OH}
   \end{array}
   \]

   f. \[
   \begin{array}{c}
   \text{Cl}
   \end{array}
   \xrightarrow{\text{KO, DMF}}
   \begin{array}{c}
   \text{CO}_2
   \end{array}
   \]

   g. \[
   \begin{array}{c}
   \text{Br}
   \end{array}
   \xrightarrow{\text{OK, CH}_3\text{CN}}
   \begin{array}{c}
   \text{H}
   \end{array}
   \]

   h. \[
   \begin{array}{c}
   \text{I}
   \end{array}
   \xrightarrow{\text{HMPA}}
   \begin{array}{c}
   \text{-}
   \end{array}
   \]

   i. \[
   \begin{array}{c}
   \text{Br}
   \end{array}
   \xrightarrow{\text{HOCH}_3}
   \begin{array}{c}
   \text{OCH}_3
   \end{array}
   \]

2. (6 pts) Name compounds a. and b.; draw the structure of compound c.: 

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

   b. \[
   \begin{array}{c}
   \text{F}
   \end{array}
   \]

   c. trans-1-chloro-3-iodocyclobutane
3. (6 pts) Place the appropriate solvent (DMSO or HOCH$_2$) under the reaction arrow for each of the following substitution reactions so that they proceed in the forward direction. Explain your choice at the right.

\[ \text{I}^- + \text{CH}_3\text{Cl} \longrightarrow \text{Cl}^- + \text{CH}_3\text{I} \]

Here we want iodide as nucleophile and chloride as a leaving group. Chloride is the stronger base, so using a polar protic solvent would stabilize it, and keep it from being an effective nucleophile for the reverse reaction.

\[ \text{Cl}^- + \text{CH}_3\text{I} \longrightarrow \text{I}^- + \text{CH}_3\text{Cl} \]

Here we want chloride as nucleophile and iodide as a leaving group. Chloride is the stronger base, so using a polar aprotic solvent would maintain its basicity and nucleophilicity for the forward reaction.

4. (21 pts) Consider the following E2 reaction:

\[ \text{Br} + \text{O} \longrightarrow \text{Br}^- + \text{OH}^- \]

d. What is the rate equation for this reaction? Rate = k[t-butyl bromide][ethoxide]

e. Using proper Lewis structures and curved arrow formalism, propose a mechanism for this process.

\[ \begin{array}{c}
\text{O}^- \\
\text{H} \\text{Br}^+ \\
\text{O}^- \\
\text{H} \\text{Br}^+ \\
\end{array} \longrightarrow \begin{array}{c}
\text{H} \\
\text{O}^- \text{H} \text{Br}^+ \\
\text{H} \\
\text{O}^- \text{Br}^+ \\
\end{array} \]

f. Draw an energy diagram. Label the axes, starting material, product, EA and $\Delta H_{\text{rxn}}$; Draw the structures of the transition states for the rate limiting step and any reactive intermediates; identify the rate limiting step.

5. (4 pts) Predict which of the following substrates would undergo E1 more rapidly. Explain your choice.

\[ \text{Br}^- \text{CH}_3 \] vs. \[ \text{CH}_3\text{CH}=	ext{CH}_2 \]

E1 reactions are faster if the intermediate carbocation is more stable. By the Hammond postulate, the transition state lowers in energy in an endothermic process if the products are more stable. The alkyl halide on the left gives a 3° carbocation; the one on the right is 3° and resonance stabilized. Therefore the one on the RIGHT is of lower energy and E1 is more rapid.
6. (4 pts) The following $S_N2$ reaction yields a product with the given empirical formula. Suggest a structure for this compound and briefly show how it formed:

$$\text{OH} \quad \text{KOH} \quad \rightarrow \quad \text{O}$$

7. (8 pts) Each of the following alkyl bromides gives only one product in E2 elimination. What is the stereochemical relationship between the two products?

$$\text{E}_2 \quad \text{E}_2$$

8. (5 pts) Cyclopropyl bromide reacts $10^4$ times slower than isopropyl bromide in an $S_N2$ reaction in a polar aprotic solvent with any given nucleophile even though both are $2^\circ$ alkyl halides. Suggest a reason for this. Possible considerations would be the mechanism, transition state, kinetics, thermodynamics or other concepts we covered in class.

For $S_N2$, stabilization of the transition state speeds the reaction. By the Hammond postulate the transition state ‘resembles’ the starting alkyl halide. Both of these are secondary. But since the cyclopropyl bromide is strained, it is at a higher potential energy, and would therefore have a higher energy transition state. Thus a slower reaction.

9. (5 pts) The $S_N1$/$S_N2$/$E1$/$E2$ reactions you have learned are very important for the understanding of biochemistry. One step in the urea cycle for ridding an organism of ammonia is the conversion of arginosuccinate to the amino acid arginine plus fumarate.
   a. What reaction is occurring here? ___E2___
   b. On the structure below show the arrow formalism for the mechanism.
   c. Draw the structure of the arginine leaving group in the space provided.

10. (5 pts) In class we used the model of hyperconjugation to explain relative carbocation stabilities. How does the data below for the relative rates of $S_N1$ reaction for the illustrated substrate support the hypothesis?

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*Relative rate means (for example) that the reaction for $R = \text{CH}_3$ is 540 times faster than the reaction for $R = (\text{CH}_3)_3\text{C}$-

When $R = \text{CH}_3$, there are three sp$^3$-C to H lobes in contact with the 2$^\circ$ carbocation, stabilizing it.
In $R = \text{CH}_3\text{CH}_2$- this decreases to 2, and to 1 in $R = (\text{CH}_3)_2\text{CH}$-
For $R = (\text{CH}_3)_3\text{C}$- there are no sp$^3$-C to H lobes at all.

Score ______/100   Approx. Course Grade: _____