1. (40 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. 

b. 

c. 

d. 

e. 

f. 

g. 

h. 

i. 

j.
2. (27 pts) Consider the following \( S_N1 \) reaction:

\[
\begin{align*}
\text{acetate} & \quad + \quad \text{Cl}^+ \quad \rightarrow \quad \text{acetic acid} \quad + \quad \text{Cl}^- \\
\end{align*}
\]

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

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

b. Draw an energy diagram.

Label:
- The axes
- Starting materials
- Products
- Transition state(s)
- \( E_{A1} \)
- \( E_{A2} \)
- \( \Delta H_{rxn} \)

Draw the structures of the transition states for the rate limiting step and any reactive intermediates.

Identify the rate-limiting step.

Rate limiting step is first one

c. What is the rate equation for this reaction?

Rate = \( k[\text{alkyl halide}] \)

d. For the reaction above, what happens to the rate of \( S_N1 \) in the following circumstances? Circle the proper answer.

i. Concentration of alkyl halide is doubled

\[ \text{Increases} \quad \text{Decreases} \quad \text{No effect} \]

ii. Concentration of acetate is doubled

\[ \text{Increases} \quad \text{Decreases} \quad \text{No effect} \]

iii. Chlorine is changed to iodine

\[ \text{Increases} \quad \text{Decreases} \quad \text{No effect} \]

iv. Chlorine is changed to fluorine

\[ \text{Increases} \quad \text{Decreases} \quad \text{No effect} \]

v. Acetic acid is changed to DMSO

\[ \text{Increases} \quad \text{Decreases} \quad \text{No effect} \]

vi. Acetic acid is changed to methanol (CH\(_3\)OH)

\[ \text{Increases} \quad \text{Decreases} \quad \text{No effect} \]

vii. Acetate is changed to methoxide (CH\(_3\)O\(^-\)) in DMSO

\[ \text{Increases} \quad \text{Decreases} \quad \text{No effect} \]

viii. Alkyl halide is changed from 3° to 2°

\[ \text{Increases} \quad \text{Decreases} \quad \text{No effect} \]

ix. Alkyl halide is changed to

\[ \text{Increases} \quad \text{Decreases} \quad \text{No effect} \]
3. (12 pts) Indicate the starting alkyl halide and conditions necessary to produce each of the following products. Indicate proper stereochemistry where necessary.

a. 
\[ \text{alkyne} \xrightarrow{\text{I}} \text{alkyne} \]

b. 
\[ \text{alkene} \text{, } X \xrightarrow{\text{t-BuOK, DMSO}} \text{only product} \]

c. 
\[ \text{alkene} \text{, } X \xrightarrow{\text{KSH, DMSO}} \text{only product} \]

4. (8 pts) Methyl tert-butyl ether (MTBE) is an anti-knock agent added to gasoline to boost octane levels. You are an industrial chemist posed with the following question. Which of the three methods below is the optimum method to synthesize MTBE with the least waste? **EXPLAIN YOUR CHOICE!**

\[ \text{Br} \xrightarrow{\text{HO-CH}_3} \text{MTBE} \]

\[ \text{O} \xrightarrow{\text{I-CH}_3} \]

\[ \text{Br} \xrightarrow{\text{HO-CH}_3} \]

First reaction will give an E2 product, not MTBE; third reaction will give mixture of MTBE and alkenes as it is SN1; second reaction will give only MTBE – although alkoxide is big and bulky, the methyl iodide cannot undergo E2 and therefore react via an SN2 pathway.

5. (7 pts) Consider the reaction below. The rate of this reaction is markedly increased if a catalytic amount of NaI (sodium iodide) is added to the reaction mixture. **Explain how the presence of iodide can speed up the rate of this reaction.**

\[ \text{alkyne-Cl} \xrightarrow{\text{NaCN, DMSO}} \text{alkyne-CN} \]

Iodide is a better LG and nucleophile.
6. (6 pts) Propose a mechanism that explains formation of the following product:

\[
\text{OH} \quad \Delta \quad \text{H}_2\text{SO}_4 \\
\text{H}_2\text{SO}_4
\]

\[
\text{OH} \quad \text{slow} \quad \text{fast} \quad \text{H}_2\text{SO}_4
\]

1,2-alkyl shift
1,2-hydride shift
this cation is resonance stabilized

Score _______/110  Approx. Course Grade:  
A  A-  B+  B  B-  C+  C  D  F