Part I

(20% for questions 1-10)

1. If the following E2 reaction proceeds through an anti-periplanar transition state, what product or products are expected?

   \[
   \text{CH}_3\text{Cl} \quad \xrightarrow{\text{KOC(CH}_3\text{)_3}} \quad \text{CH}_3\text{COH}
   \]

   A) only 1-methylcyclohexene
   B) only 3-methylcyclohexene
   C) only 4-methylcyclohexene
   D) equal amounts of 1-methylcyclohexene and 3-methylcyclohexene

2. Zaitsev's rule can be used to predict the major product for which of the following reactions?

   A) 2-methylpentane + Br₂ (with light)
   B) 2-bromo-2-methylpentane + NaOCH₂CH₃ (in ethanol)
   C) 2-methyl-2-pentanol + PBr₃
   D) 2-methyl-2-pentanol + HCl

3. Which reaction sequence below would work best in converting 3-pentanol into 2,3-dibromopentane?

   A) (1) H₂SO₄, heat (2) HBr (3) Br₂, light
   B) (1) H₂SO₄, heat (2) H₂/Pt (3) 2 Br₂, light
   C) (1) Br₂, light (2) H₂SO₄, heat (3) H₂/Pt
   D) (1) H₂SO₄, heat (2) Br₂

4. Which of the following C₆H₁₀ cycloalkenes would give a pair of diastereomeric epoxides when reacted with peroxyacetic acid, CH₃C₀₂H?

   A) 1-methylcyclopentene
   B) 3-methylcyclopentene
   C) 1,2-dimethylcyclobutene
   D) 3,3-dimethylcyclobutene

5. Which of the following is not true concerning the addition of HCl to 1,3-butadiene?

   A) The intermediate is an allylic carbocation.
   B) A carboxylation rearrangement leads to the 1,4-addition product.
   C) The 1,4-addition product is the thermodynamically controlled product.
   D) The reaction mechanism has two steps.

6. Select the best method to carry out the following conversion.

   \[
   \text{HC}≡\text{CCH}_2\text{CH}_2\text{CH(CH}_3\text{)}_2 \quad \xrightarrow{\text{?}} \quad \text{HOCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH(CH}_3\text{)}_2
   \]

   A) (1) H₂O, H₂SO₄/HgSO₄ (2) H₂/Pt
   B) (1) HBr (2) H₂/Pt (3) NaOH
   C) (1) H₂, Lindlar Pd (2) BH₃/THF (3) H₂O₂, NaOH
   D) (1) HBr, peroxides (2) NaOH (3) H₂, Pt
7. Propylbenzene is subjected to the sequence of reactions below. What is the final product?

\[
\begin{align*}
\text{CH}_3\text{CH}_2\text{CH}_3 & \quad \text{Br}_2 \quad \text{Br} \quad \text{KOC(CH}_3)_3 \quad \text{Br} \quad \text{HBr} \\
\text{hv} & \quad \text{(CH}_3)_2\text{COH} \quad \text{peroxides} \\
\text{A)} & \quad \begin{array}{c}
\text{CH}_3\text{CH}_2\text{CH}_2\text{OH} \\
\text{Br} \\
\text{B)} & \quad \begin{array}{c}
\text{CH}_3\text{CH}_2\text{CH}_3 \\
\text{Br} \\
\text{C)} & \quad \begin{array}{c}
\text{CH}_3\text{CH}_2\text{CH}_2\text{Br} \\
\text{Br} \\
\text{D)} & \quad \begin{array}{c}
\text{CH}_3\text{CH}_2\text{CH}_2\text{Br} \\
\text{Br}
\end{array}
\end{array}
\end{array}
\end{align*}
\]

8. Which one of the following compounds has the fastest S_N1 reaction rate with H_2O in acetone?

\[
\begin{align*}
\text{A)} & \quad \begin{array}{c}
\text{CH}_3 \quad \text{CH}_3 \\
\text{H}_3\text{C} - \text{Cl} \\
\text{OCH}_3 \\
\text{B)} & \quad \begin{array}{c}
\text{CH}_3 \quad \text{CH}_3 \\
\text{H}_3\text{C} - \text{Cl} \\
\text{CH}_3 \\
\text{C)} & \quad \begin{array}{c}
\text{CH}_3 \quad \text{CH}_3 \\
\text{H}_3\text{C} - \text{Cl} \\
\text{NO}_2 \\
\text{D)} & \quad \begin{array}{c}
\text{CH}_3 \quad \text{CH}_3 \\
\text{H}_3\text{C} - \text{Cl} \\
\text{IV}
\end{array}
\end{array}
\end{array}
\end{align*}
\]

9. What is the multiplicity of the methylene hydrogens indicated in the proton NMR of the following compound?

\[
\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_3
\]

\[
\begin{align*}
\text{A)} & \quad \text{singlet} \\
\text{B)} & \quad \text{doublet} \\
\text{C)} & \quad \text{triplet} \\
\text{D)} & \quad \text{quartet}
\end{align*}
\]
10. Starting with toluene, which of the following is the best method to make the ether shown below? (Assume you can separate ortho and para isomers.)

A) \[
\begin{align*}
\text{NBS, heat benzoyl peroxide} & \quad \text{Cl}_2/\text{FeCl}_3 \\
\end{align*}
\]

B) \[
\begin{align*}
\text{Cl}_2/\text{FeCl}_3 & \quad \text{NBS, heat} \\
\end{align*}
\]

C) \[
\begin{align*}
\text{NBS, heat benzoyl peroxide} & \quad \text{NaOH, H}_2\text{O} \\
\end{align*}
\]

D) \[
\begin{align*}
\text{Cl}_2/\text{FeCl}_3 & \quad \text{NBS, heat benzoyl peroxide} \\
\end{align*}
\]

11. Write the major product of the following reactions. (8%)

A \[
\begin{align*}
\text{O} & \quad \text{NH}_3, \text{NaBH}_3\text{CN} \\
\end{align*}
\]

1. excess CH\textsubscript{3}I
2. Ag\textsubscript{2}O, H\textsubscript{2}O, heat

B \[
\begin{align*}
\text{CH}_2\text{CN} & \quad (\text{CH}_3)_2\text{NH} \\
\end{align*}
\]

12. Write the major product of the following reactions. (8%)

A \[
\begin{align*}
\text{O} & \quad \text{LiAlH}_4, \text{then H}_3\text{O}^+ \\
2. \text{PBr}_3 & \\
\end{align*}
\]

1. Mg, ether
2. CH\textsubscript{2}O

B \[
\begin{align*}
\text{O} & \quad \text{POCl}_3, \text{pyridine} \\
\end{align*}
\]

C \[
\begin{align*}
\text{O} & \quad \text{PCC} \\
2. \text{C}_6\text{H}_5\text{CH}_2\text{MgBr} & \\
\end{align*}
\]
Part II
1. Choose the best answer for each of the following questions: (6%)
   i) Which of the following Friedel–Crafts alkylations won’t work as written?
      (a) \[
      \text{C}_6\text{H}_5 + \text{CH}_2\text{Cl} \xrightarrow{\text{AlCl}_3} \text{C}_6\text{H}_5\text{CH}_2\text{Cl} \]
      (b) \[
      \text{C}_6\text{H}_5 + \text{CHCl}_3 \xrightarrow{\text{AlCl}_3} \text{C}_6\text{H}_5\text{CHCl}_3 \]
      (c) \[
      \text{O}_2\text{NCH} + \text{CH}_2\text{Cl} \xrightarrow{\text{AlCl}_3} \text{O}_2\text{NCHCH}_2\text{Cl} \]
      (d) \[
      \text{H}_3\text{CO} + \text{C}_5\text{H}_4\text{Cl} \xrightarrow{\text{AlCl}_3} \text{H}_3\text{CO} \text{C}_5\text{H}_4\text{Cl} \]
      (A) b (B) c (C) a and d (D) b and c (E) c and d

   ii) Which of the following compounds or chemical entities are aromatic?
      (a) \[
      \text{S} \]
      (b) \[
      \text{C}_6\text{H}_6 \]
      (c) \[
      \text{CH}_3\text{C} \]
      (d) \[
      \text{C}_5\text{H}_5 \]
      (e) \[
      \text{O}_2\text{N} \]
      (A) a and b (B) d and e (C) a, b, and c (D) b, c, and d (E) a, c, and e

2. Does the MO energy diagram of cyclooctatetraene appear to be a particularly stable or unstable configuration? Explain. (5%)

3. Phenolphthalein (structure shown below) is a common acid-base indicator that is colorless when neutral, but turns a magenta color when treated with base due to a rearrangement of the atoms in the molecule. Propose a reasonable structure for this indicator which can show a magenta color. (4%)

\[
\text{phenolphthalein (colorless)} \xrightarrow{\text{base}} \text{phenolphthalein (magenta)}
\]
4. Using a 60 MHz $^1$HNMR spectrometer, a chemist observes the following absorption: (6%)
doublet, $J = 7$ Hz, at 4.00 ppm
(a) What would the chemical shift be in the 300 MHz spectrum?
(b) What would the coupling constant be in the 300 MHz spectrum?
(c) How many hertz from the TMS peak is this absorption in the 60 MHz spectrum?

5. Mustard gas, ClCH$_2$CH$_2$SCH$_2$CH$_2$Cl, was used as a poisonous chemical agent in World War I. Mustard gas is much more toxic than a typical primary alkyl chloride. Its toxicity stems from its ability to alkylate amino groups on important metabolic enzymes, rendering the enzymes inactive.
(a) Propose a mechanism to explain why mustard gas is an exceptionally potent alkylating agent. (5%)
(b) Bleach (sodium hypochlorite, NaOCl) neutralizes and inactivates mustard gas. Propose products that might be formed by the reaction of mustard gas with bleach. (4%)

Part III
1. Please predict the products of the following reactions. (5%)

2. Please predict the structures of the following synthetic route. (3%)

3. Identify the reagents represented by the letters A-E in the following scheme: (5%)

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4. How would you carry out the following transformation? (3%)

\[ \text{A} \rightarrow \text{B} \]
\[ \text{B} \rightarrow \text{C} \]

5. Identify the reagents A-E in the following scheme: (5%)

6. When crystal of pure \( \alpha \)-mannose are dissolved in water, isomerization slowly occurs to produce \( \beta \)-mannose. Propose a mechanism for the isomerization. (5%)

7. Fill in the reagents A-H in the following scheme: (8%)