Part I - Chapters 1 through 4 and 12 (64 points)

1. Mifepristone, also known as "RU 486", is a contragestive that was approved not long ago for use in the United States. It terminates pregnancy by interfering with the gestation of a fertilized ovum. Label the indicated atoms in mifepristone with the correct hybridization. (5 points)
2. In the dipeptide glylyglycine, shown below, the nitrogen atom in the peptide linkage has bond angles of about 120°, consistent with sp^2 hybridization, however, the nitrogen in the free amine group has bond angles close to 109°, consistent with sp^3 hybridization. Provide a brief rational for the difference. (4 points)

The nitrogen in the peptide linkage hybridizes sp^2 to allow conjugation to the carbonyl.

3. For each of the following partial Lewis structures of neutral compounds, add non-bonding electrons and multiple bonds as needed to complete the Lewis structure. Then draw an alternate resonance form for each structure which conforms to the octet rule. Include formal charges as appropriate. (16 points)
4. Draw a Newman projection of the most stable conformation of the hydrocarbon on the left sighting down the bond indicated by the arrow. Draw the hydrocarbon on the right in its most stable chair conformation. (8 points)

5. A sample bottle on the lab shelf contains an organic liquid with a label that reads "dichloropropane", but whoever labeled it forgot to indicate whether it was 1,1-dichloropropane, 1,2-dichloropropane, 1,3-dichloropropane, or 2,2-dichloropropane. Use the $^1H$ NMR spectrum on the following page to determine which compound it is and circle the correct compound. Draw an arrow from each carbon atom of the correct structure to the NMR signal that represents the hydrogens on that carbon. (Note: The circled numbers on the NMR spectrum show the integration value for each signal in smallest whole number ratio.) (6 points)
5. (continued)

300 MHz $^1$H NMR
In CDCl$_3$
6. Draw structures of the major organic product(s) of the following reactions. If the reaction gives a specific stereoisomer, be sure to show the correct one. (4 points each)

Note: This reaction is a syn dihydroxylation which only gives (R,R) and (S,S) product (no Rs or Sr) but we had not covered this before Exam I.

\[ \text{alkene} \xrightarrow{\text{KMnO}_4, \text{OH}^-, \text{cold}} \text{OH} \]

\[ \text{H}_2 \xrightarrow{\text{Pt}} \text{cyclohexane} \]

\[ \text{alkene} \xrightarrow{\text{H}_2\text{O}, \text{H}^+} \]

\[ \text{alkyne} \xrightarrow{\text{HBr}, \text{(excess)}} \]

\[ \text{alkene} \xrightarrow{1. \text{BH}_3, 2. \text{H}_2\text{O}_2, \text{OH}^+} \]

\[ \text{alkene} \xrightarrow{\text{Br}_2, \text{(1 equivalent)}} \]
Part II – Chapters 5 through 9 (70 points)

1. Draw structures for the following compounds: (8 points)

Butyl methyl ether

(Z)-3-chloro-3-hexene

(S)-2-bromopentane

3,4-dimethylpentanal

2. Nitration of acetophenone using a mixture of nitric and sulfuric acids proceeds at room temperature to form m-nitroacetophenone in high yield as shown in the following reaction equation. (Continued on next page.)
2. (continued)

A. Draw a stepwise mechanism for the reaction using curved arrows to show the movement of electron pairs in each step. Be sure to show how the electrophile is formed and show structures for any intermediates. (8 points)

\[
\text{Formation of electrophile:} \quad \text{O} - \text{N} = \text{O} \quad \text{H}_2\text{O}
\]

B. Draw three resonance structures for the acetophenone starting compound to demonstrate why substitution at the meta position is favored and briefly explain how the resonance structures predict meta substitution. (8 points)

Those contributing resonance forms place positive charge on ortho and para positions making them less favorable (than meta) for electrophilic attack by \( \text{NO}_2^+ \).
3. Cortisone (structure shown below) is a steroid that is widely used in treatment of arthritis and other medicinal applications where it is used to reduce inflammation related to allergic response. Label each stereocenter in cortisone as R or S. (R points)
5. For each of the following reactions, draw the structure of the major product. If the major product is one specific stereoisomer, be sure to show the correct stereochemistry. If the major product is formed as a pair of enantiomers (racemic mixture), indicate that. It is not necessary to draw both enantiomers. (4 points each = 32 points)
\[
\text{Br} \quad \text{CH}_3O^\ominus \quad \text{CH}_2\text{CH}_3 \quad \text{Br}
\]

\[
\text{Br}_2 \quad \text{(excess)} \quad E_A S
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\text{Br} \quad \text{Br}
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6. For full credit on this problem, show a synthesis of the compound shown below using an aldol reaction and other reactions if necessary to arrive at the final product. The organic starting materials must be aldehydes and/or ketones with five carbons or less. (8 points)

For partial credit, you can show a synthesis of the compound using any aldehyde or ketone and a Grignard reagent. (4 points)
Part II – Chapters 10, 11, 15 through 18 (66 points)

1. The reaction below shows the formation of N-methylbenzamide from reaction of methyl benzoate with methylamine. Draw a step-wise mechanism for this reaction using curved arrows to show the movement of electron pairs in each step. Be sure to show all intermediates formed on the way to the product. (8 points)
2. For the sugar molecule, D-mannose, shown in open chain form as a Fischer projection, draw the β-anomer of the corresponding hemiacetal form (six membered pyranose ring form) in its most stable chair conformation. (4 points)

3. For the following mono and disaccharides, circle the ones that are reducing sugars. (4 points)
4. For each of the following reactions, draw the structure of the major organic product(s). (4 points each = 16)

\[
\text{\begin{align*}
\text{\textbf{Problem 1:}} & \quad \text{PhCO}_2\text{H} & \begin{array}{c}
1. \text{Cl}_2\text{SO}\text{Cl}_2 \\
2. \text{CH}_3\text{NH}_2 \text{ (excess)}
\end{array} \quad \text{PhCONH}_2 \\
\text{\textbf{Problem 2:}} & \quad \text{PhCH}_2\text{CH}_2\text{Br} & \begin{array}{c}
1. \text{HN(\text{CH}_2}_2 \\
2. \text{NaOH}
\end{array} \\
\text{\textbf{Problem 3:}} & \quad \text{PhCO}_2\text{Ph} & \begin{array}{c}
\text{H}^+ \\
\text{H}_2\text{O}
\end{array} \\
\text{\textbf{Problem 4:}} & \quad \text{PhCH}_2\text{CH}_3 & \begin{array}{c}
1. \text{CH}_3\text{NH}_2 \\
2. \text{NaBH}_4
\end{array}
\end{align*}}
\]
5. For each of the following syntheses, provide reagents over the arrow that would convert the starting material to the product shown, in good yield. Some of the syntheses might require more than one step. If more than one step is required, show the reagents separately for each step numbering them 1, 2, etc. (4 points each = 8)

\[
\text{Ph-CH} = \text{CO} \quad \xrightarrow{H^+ \text{c. H}_2 \text{CH}_2 \text{OH}} \quad \text{Ph-CH} = \text{CH-CH}_2 \text{OH}
\]

\[
\text{Ph-CH} = \text{CO} \quad \xrightarrow{1) \text{SOCl}_2} \quad \text{Ph-CH} = \text{CH-CH}_2 \text{Cl} \quad \xrightarrow{2) \text{CH}_3 \text{NH}_2} \quad \xrightarrow{3) \text{LiAlH}_4} \quad \text{Ph-CH} = \text{CH-CH}_2 \text{NHCH}_3
\]

6. Draw a complete structure for the tripeptide, Ser-Ala-Asp. Show correct stereochemistry at each stereocenter. (6 points)

\[
\text{H}_2 \text{N-CH} = \text{CHCOO}^- \quad \text{H} \quad \text{CH}_3 \quad \text{H} \quad \text{N-COO}^- \quad \text{H} \quad \text{CH}_3 \quad \text{N-H}
\]

7. The isoelectric point of lysine is 9.7. Draw the major ionic form of lysine that is present in aqueous solution at pH=9.7. (3 points)

\[
\text{H}_2 \text{N-CO}^- \quad \text{H} \quad \text{N-CH} = \text{CH}_{\text{C}}^+ \text{H}_3 \text{N}^+ \text{H}_2\text{O}
\]
8. Briefly describe what is meant by each of the following levels of protein structure: (8 points)

Primary structure: The amino acid sequence.

Secondary structure: Conformation of the protein backbone over relatively short distances determined by peptide bond geometry and highly ordered hydrogen bonding (e.g., α-helix, β-sheet)

Tertiary structure: Overall 3-D structure of protein including twisting and folding due to hydrogen bonding, hydrophobic interactions, etc.

Quaternary structure: Higher order structure resulting from combination of protein subunits (e.g., 4 subunits in hemoglobin)
9. Using the compounds shown below, draw the structure of a dinucleotide of DNA containing a purine and a pyrimidine base. (8 points)