This exam has nine (9) questions. Please check before beginning to make sure no questions are missing. All scratch work must be done on the attached blank pages, which will be collected. Please sign BOTH cover pages.
Periodic Table of the Elements

<table>
<thead>
<tr>
<th>Group</th>
<th>Period</th>
<th>Elements</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>1</td>
<td>H, He</td>
</tr>
<tr>
<td>II</td>
<td>2</td>
<td>Li, Be</td>
</tr>
<tr>
<td>III</td>
<td>3</td>
<td>Na, Mg, Transition elements</td>
</tr>
<tr>
<td>IV</td>
<td>4</td>
<td>K, Ca, Se, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge, As, Se, Br, Kr</td>
</tr>
<tr>
<td>V</td>
<td>5</td>
<td>Rb, Sr, Y, Zr, Nb, Mo, Tc, Ru, Rh, Pd, Ag, Cd, In, Sn, Sb, Te, I, Xe</td>
</tr>
<tr>
<td>VI</td>
<td>6</td>
<td>Cs, Ba, La, Hf, Ta, W, Re, Os, Ir, Pt, Au, Hg, Tl, Pb, Bi, Po, At, Rn</td>
</tr>
<tr>
<td>VII</td>
<td>7</td>
<td>Fr, Ra, Ac</td>
</tr>
<tr>
<td>O</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**ADVICE:** A picture is worth a thousand words!
1. Upon free radical bromination, 2-methylpropane gives a mixture of products consisting of 99% 2-bromo-2-methylpropane and 1% 1-bromo-2-methylpropane. Explain this selectivity by filling in the energy diagram below (you need only show the rate-determining step). (10 pts).

[Energy diagram with labels and reaction progress]

2. An optically active bromoalkane A was reacted with an unknown carbanion B to give an enantiomerically pure product C of molecular formula C₇H₁₂. On catalytic hydrogenation C absorbed two equivalents of hydrogen to give enantiomerically pure D having the S-configuration. Ozonolysis of C produced acetic acid (CH₃CO₂H) and an optically active carboxylic acid E of molecular formula C₅H₁₀O₂. Provide the structures for A-E, including absolute stereochemistry where appropriate, and show the reactions involved. (10 pts).
3. Provide the most efficient synthesis possible for each of the following materials from the indicated starting compounds. Read the question carefully. There will be no credit given for preparing the correct product from incorrect starting materials, or for preparing an incorrect product from correct starting materials.

(a) 1-Bromo-2-chloro-4-methylpentane from 2-bromopropane and any inorganic reagents of your choice. (10 pts).

(b) trans-1-Hydroxy-3-methylcyclopentane from cyclopentane, methane, and any inorganic reagents of your choice. (10 pts)

4. (a) Show three-dimensional structures for all possible isomers of dimethylcyclopropane. Circle the isomers that are chiral. (10 pts).

(b) If a mixture containing equal amounts of these isomers was subjected to simple chromatography, how many fractions would be obtained? Identify each fraction (5 pts).

THREE FRACTIONS: A (meso), B (meso) AND C + D (INSEPARABLE ENANTIOMERS)

(c) How many of the fractions from (b) above would be optically active? (5 pts).

NONE
5. (a) For each pair of compounds below circle the one that will undergo \( S_N^2 \)-substitution more rapidly. Explain your choice in 2-3 words and with accurate drawings (8 pts).

   ![Diagrams of compounds for \( S_N^2 \) reaction]

   unhindered approach of nucleophile blocked unhindered approach of nucleophile blocked

(b) For each pair of compounds below circle the one that will undergo E2-elimination more rapidly. Explain your choice in 2-3 words and with accurate drawings (8 pts).

   ![Diagrams of compounds for E2 reaction]

   proper anti-periplanar geometry

   \( "I \) better leaving group

6. Provide Fischer projections for all products of mono-bromination of \((S)-2\)-bromopentane at each carbon atom. For each product, specify whether they are chiral or achiral, whether they are formed in equal or unequal amounts, and whether they are optically active. (14 pts).

   ![Fischer projections for mono-bromination]

   \((S)-2\)-bromopentane

   C-1 attack: Chiral, optically active

   C-2 attack: Achiral

   C-3 attack: Chiral, optically active diastereomers formed in unequal amounts

   C-4 attack: Achiral, meso optically inactive

   C-4 attack: Chiral, optically active diastereomer formed in unequal amount

   C-5 attack: Chiral, optically active
7. Predict the major product, including stereochemistry where applicable, for each reaction indicated below. You must draw your answer neatly in the box to receive credit. (20 pts).

(a) \((2R,3S)-2\text{-Bromo-3-phenylbutane} + \text{KOH/EtOH}\)

(b) \(\text{NaCN} + (S)-1\text{-deutero-1-bromopropane}\)

(c) \((\text{CH}_3)_3\text{C}^-\text{Na}^+ + 2\text{-chloro-2,3-dimethylbutane}\).

(d) \(\text{trans-1-Bromo-2-methylcyclohexane} + \text{KOH/EtOH}\)
8. In contrast to S_N2 reactions, S_N1 reactions show relatively little selectivity for nucleophiles of different strengths. (a) Illustrate the reason for this difference by filling in the energy diagram below, using any alkyl halides and nucleophiles of your choice. Clearly label all intermediates and transition states. (10 points).

(b) Explain how your answer to (a) above accounts for the fact that \( \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2^-\text{Cl} \) reacts with 0.01 M NaCN in EtOH to yield primarily \( \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2^-\text{CN} \), while under the same conditions \( \text{(CH}_3\text{)}_3\text{C-Cl} \) gives primarily \( \text{(CH}_3\text{)}_3\text{C-OEt} \). (5 points).

CH\(_3\)CH\(_2\)CH\(_2\)CH\(_2^-\)Cl reacts by an S\(_\text{N2}\) mechanism, which favors the stronger nucleophile CN even though it is present in much lower concentration. (CH\(_3\))\(_3\)C-Cl reacts by an S\(_\text{N1}\) mechanism, and the high energy carbocation intermediate reacts fastest with the nucleophile present in highest concentration (EtOH), even though it is weak.

9. Circle the compounds drawn below that are chiral. (15 pts).