This exam has six (6) 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, B, C, N, O, F, Ne</td>
</tr>
<tr>
<td>III</td>
<td>3</td>
<td>Na, Mg, Al, Si, P, S, Cl, Ar</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, 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>
</tbody>
</table>

#### Lanthanide Series
- Ce, Pr, Nd, Pm, Sm, Eu, Tb, Dy, Ho, Er, Tm, Yb, Lu
- Elements 58 to 71

#### Actinide Series
- Th, Pa, U, Np, Pu, Am, Cm, Bk, Cf, Es, Fm, Md, No, Lw
- Elements 90 to 103

**Advice:** A picture is worth a thousand words!
1. (a) Circle the compounds drawn below which you would expect to exhibit "aromatic" character. (15 pts).

(b) The dipole moment for the compound drawn below is considerably larger than one might expect for a structure of this type. Obviously there is a contributing resonance hybrid which better accommodates this fact. Provide the structure for this hybrid and clearly indicate the direction of the dipole moment. (5 pts).

2. (a) Heterolysis of pure 3-bromo-1-butene at 40° C provides a mixture consisting of 80% 1-bromo-2-butene and 20% 3-bromo-1-butene. The same mixture is obtained upon heterolysis of pure 1-bromo-2-butene at 40° C. Rationalize this observation by filling in the energy diagram below, clearly showing the structure and relative energies of all species involved. (15 pts).
(b) Account for the fact that 2-methyl-1,3-butadiene reacts with HCl to yield only 3-chloro-3-methyl-1-butene and 1-chloro-3-methyl-2-butene. (10 pts).

\[
\begin{align*}
\text{Me} & \quad \text{H}^+ \\
\begin{array}{c}
\text{Me} \\
\text{H} \\
\text{Me} \\
\text{H}
\end{array} & \quad \leftrightarrow \\
\begin{array}{c}
\text{Me} \\
\text{H} \\
\text{Me} \\
\text{H}
\end{array} & \quad \rightarrow \\
\begin{array}{c}
\text{Me} \\
\text{Cl} \\
\text{H} \\
\text{Cl}
\end{array} & + \\
\begin{array}{c}
\text{Me} \\
\text{Cl}
\end{array}
\end{align*}
\]

3°-Allylic carbocation formed by protonation at C-1 is most stable of four possible intermediates

3. (a) Three isomeric dimethylcyclopropanes give, respectively, two, three, and four NMR signals in an achiral solvent. Provide accurate drawings for the isomer giving rise to each number of signals. (6 pts).

(b) What is a likely structure for a hydrocarbon of formula C₆H₁₂ that shows strong absorption at 2920, 2840 and 1450 cm⁻¹; but no absorption above 2920 cm⁻¹ and no absorption in the 1650 cm⁻¹ range? (4 pts).

(c) There are several possible isomers having molecular formula C₄H₈Br₂. One of them (compound A) has the NMR absorptions shown below. Deduce the structure of A and briefly explain your logic (1-2 sentences maximum). (5 pts).

**A:** 1.7 (doublet, 3H), 2.3 (quartet, 2H), 3.5 (triplet, 2H), 4.2 (multiplet, 1H)

Chemical shifts and splitting patterns are consistent with structure A. The 3 proton doublet at 1.7 is particularly diagnostic, as well as the 2 proton triplet at 3.5.
(d) Account for the fact that the CH₃ group (B) absorbs at considerably higher magnetic field in the NMR spectrum than CH₃ group (A). (5 pts).

![Diagram of molecular structures](image)

B is in the shielding zone of the benzene ring

4. Provide a brief explanation for the following experimental observations.

(a) cis-4-tert-Butylcyclohexylbromide (A) reacts rapidly with NaOEt in EtOH to yield 4-tert-butylcyclohexene; the rate of reaction is proportional to the concentration of both A and NaOEt. Under the same conditions, trans-4-tert-butylcyclohexylbromide (B) reacts slowly to yield the same alkene; the rate of reaction depends only on the concentration of B. (12 pts).

![Diagram of reaction mechanisms](image)

(b) The heat of hydrogenation for converting 1,4-dimethyl-1,3-cyclohexadiene to 1,4-dimethylcyclohexane is less than the heat of hydrogenation for converting 1,3-dimethyl-1,3-cyclohexadiene to 1,3-dimethylcyclohexane. (Assume both starting materials are of equal stability). (10 pts).

![Diagram of energy changes](image)

(less stable - smaller ΔH°)
5. 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. (55 pts).

a) \( \text{CH}_3-\text{C}=\text{CH-CH}_2-\text{CH}=\text{CH-CO}_2\text{Me} \rightarrow \text{H}_3\text{C}\text{CH}_3\text{CO}_2\text{Me} \)

b) \( \text{Me}+\text{CO}_2\text{Me} \rightarrow \text{MeCO}_2\text{Me} \)

c) \( \text{CH}_3-\text{C}=\text{C}^+\text{Na}^+ + 2\text{-chloro-2-methylbutane} \)

d) \( \text{Me}+\text{MeCO}_2\text{Me} \rightarrow \text{MeCO}_2\text{Me} \)

e) \( 3,4\text{-dimethyl-trans-3-hexene} + \text{H}_2 / \text{Pd} \rightarrow \text{CH}_3\text{CH}_2\text{CH}_3\text{CH}_3\text{CH}_2\text{CH}_3\text{CH}_3\text{CH}_2\text{CH}_3\text{CH}_3\text{CH}_2\text{H} \)
f) \( \text{Cyclopentene} + \text{Ph} \rightarrow \text{H}_2 \text{Pd/25 °C} \)

\[
\text{Ph} \quad \text{H} \\
\text{H} \quad \text{H} \\
\text{H} \\
\text{Ph} \quad \text{H} \\
\text{H} \\
\]

\[
\begin{array}{c}
\text{Ph} \\
\text{H} \quad \text{H} \\
\text{H} \\
\text{Ph} \\
\text{H} \\
\end{array}
\]

g) \( \text{Me-ethylene} + \text{furane} \rightarrow \)

\[
\begin{array}{c}
\text{Me} \\
\text{Me} \\
\end{array}
\rightarrow
\begin{array}{c}
\text{Me} \\
\text{Me} \\
\end{array}
\]

h) \( R-3\)-Bromocyclohexene + methanol/\( \Delta \) (no base) \( \rightarrow \)

\[
\begin{array}{c}
\text{OMe} \\
\text{Me} \\
\end{array}
\]
(nearly racemic)

i) \( 1\)-Methylcyclohexene + \( \text{Br}_2 \)/\( \text{H}_2\text{O} \)

\[
\begin{array}{c}
\text{Br} \\
\text{CH}_3 \\
\text{Br} \\
\end{array}
\rightarrow
\begin{array}{c}
\text{Br} \\
\text{CH}_3 \\
\text{Br} \\
\end{array}
\]

j) \( 1,3\)-dimethylcyclopentene + OsO₄, then \( \text{NaHSO}_3 \)

\[
\begin{array}{c}
\text{CH}_3 \\
\text{H}_3\text{C} \\
\end{array}
\rightarrow
\begin{array}{c}
\text{CH}_3 \\
\text{H}_3\text{C} \\
\end{array}
\]

k) \( \text{trans-2-Butene} + \text{Cl}_2 \)/excess LiBr.
6. Provide the most efficient synthesis possible for each compound shown below, using the indicated starting materials and any other reagents of your choice. Neither synthesis requires more than three steps. (18 pts).

a) \[ \text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2 \quad \rightarrow \quad \text{N}=\text{C}-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\cdot \text{C}=\text{N} \]

\[ \begin{align*}
\text{Br}_2 & \quad \Delta \\
\text{BrCH}_2\text{C}=\text{C}-\text{CH}_2\text{Br} & \quad 2 \text{ NaCN} \\
\text{H}_2 & \quad \text{Pd}
\end{align*} \]

b) \[ \text{CH}_2=\text{CH}-\text{CO}_2\text{Me} \quad ; \quad \text{CHO} \]

\[ \begin{align*}
\text{CHO} & \quad \text{CO}_2\text{Me} \\
\text{CHO} & \quad \text{CO}_2\text{Me}
\end{align*} \]