MIDTERM #3
PRACTICE TEST #1

Interaction Energies, kcal/mol

<table>
<thead>
<tr>
<th></th>
<th>H/H</th>
<th>Me/Me</th>
<th>Me/Me</th>
<th>Et/Me</th>
<th>i-Pr/Me</th>
<th>t-Bu/Me</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eclipsing</td>
<td>1.0</td>
<td>~1.4</td>
<td>~2.6</td>
<td>~0.95</td>
<td>~1.1</td>
<td>~2.7</td>
</tr>
<tr>
<td>Gauche</td>
<td></td>
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</tbody>
</table>

Approximate Coupling Constants, J (Hz), for $^1$H NMR Spectra

- Aromatic: $\delta$, ppm
- Alkyl: $\delta$, ppm
- Alkyl: range of values
- Variable and condition

Infrared Correlation Chart

- $\nu$ (cm$^{-1}$)
- Broad range
- Small range
- Broad peak
- Broad with spikes
- Usual strong

NMR Correlation Charts

- Aromatic: $\delta$, ppm
- Alkyl: $\delta$, ppm
- Variable and condition
- Alkaline

TIP: Use molecular models and clarify your answers.
Question 1: Give a IUPAC name for the following structure.

![Chemical structure image]

3-ethyl-2-methyl-3-heptene

OR
3-ethyl-2-methylhept-(3Z)-ene

Question 2

a) Indicate the stronger and weaker BRONSTED acids and bases on each side of the equilibrium and which has the larger and smaller pKa

b) Draw the curved arrow pushing showing bond breaking/forming for both directions.

c) Identify the side on which the equilibrium would lie, which reaction is FASTER and give a BRIEF explanation.

d) Draw a reaction energy diagram with properly labelled axes that includes the activation energy for reaction in EACH DIRECTION and a drawing of the transition state, clearly indicates the positions on the diagram of both sets of reactants and the transition state.

\[ \text{Na}^+ : \text{Cl}^- + \text{H}^- : \text{I}^- \quad \rightleftharpoons \quad \text{H}^- : \text{Cl}^- + \text{Na}^+ : \text{I}^- \]

The H-I bond is weaker than the H-Cl bond due to larger atomic size; H-I is thus the stronger acid; the stronger acid has the smaller pKa and the weaker conjugate base.

The stronger acid/base react faster than the weaker acid/base.
Question 3: Rank the three indicated Nitrogens Na (which is not sodium!), Nb and Nc in order of increasing Bronsted BASE strength, give a BRIEF explanation for your choice.

\[ \text{weakest base} < \text{ } \text{ } \text{ } < \text{strongest base} \]

Question 4: Give a curved arrow-pushing mechanism for the following reaction, indicate the Lewis acid and base at each step and whether they are also Bronsted acid/base reactions. Draw a reaction energy diagram (no need to draw the transition states), clearly indicate the activation energy for the rate determining step and the positions of the transition states and give the number of sets of intermediates and transition states in the mechanism.
Question 5: Provide the missing major organic products or reagents/conditions for the following reactions. Assign each reaction as addition, rearrangement, substitution or elimination. Include all non-bonding electrons in the organic structures. Pay attention to relative stereochemistry as appropriate.

a) \( \text{H}_2\text{SO}_4 \text{ (cat.)} / \text{heat} \)

b) \( \text{Pd/C} \)

c) \( \text{Br}_2 / \text{hv} \)

d) \( 1. \text{BH}_3 \cdot \text{THF} \)
\( 2. \text{NaOH} / \text{H}_2\text{O}_2 \)

e) \[ \text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2 \rightarrow \text{CH}_3-\text{CH}-(\text{CH}_2)_2-\text{OH} \]
Question 6. Provided are spectra for a compound with molecular formula $C_7H_{14}O_1$.
determine the structure by answering the questions below

a) Give the degrees of unsaturation ________________

b) On the infrared spectrum, indicate the peaks that identify the functional groups in the
molecule (including C(sp$^3$)-H). Indicate **BOTH the functional group**, and where appropriate,
the specific **BOND** in the functional that corresponds to the peak.

![Infrared Spectrum]

<table>
<thead>
<tr>
<th>Wavenumber</th>
<th>Peak</th>
</tr>
</thead>
<tbody>
<tr>
<td>3345</td>
<td></td>
</tr>
<tr>
<td>2991</td>
<td></td>
</tr>
<tr>
<td>2932</td>
<td></td>
</tr>
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<td>2855</td>
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<tr>
<td>1458</td>
<td></td>
</tr>
<tr>
<td>1366</td>
<td></td>
</tr>
<tr>
<td>1155</td>
<td></td>
</tr>
</tbody>
</table>

![Proton NMR Spectrum]

3H singlet
2H triplet
H1, 2H multiplets
6H doublet

(c) draw the structure and clearly indicate which hydrogens correspond to which signals **in the
proton nmr spectrum ONLY**
Question 1: Give an IUPAC name for the following structure.

![Structure Image]

Question 2. Below are two reactions we will study in detail later in the semester.

a) Add the missing curved arrows that show bond making and bond breaking.

b) Indicate the Lewis acid and base for each reaction (LA/LB) and whether they are also Bronsted acids/bases (BA/BB).

c) The reactions are both exothermic, based on the structures of the two alkene products. Which would you expect to be most exothermic, AND, which would you expect to be faster, your explanation should include the term "Hammond postulate".

d) Draw the transition state for reaction A ONLY and indicate which reaction would have the earlier and which the later transition state on an energy versus reaction coordinate plot, and briefly explain why (just a few words needed here but mention the Hammond postulate).

![Reaction Images]
Question 3. For the following equilibrium

a) Indicate the stronger and weaker BRONSTED acids and bases on each side of the equilibrium and which has the larger and smaller pKa

b) Draw the curved arrow pushing showing bond breaking/forming for both directions.

c) Identify the side on which the equilibrium would lie, which reaction is FASTER and give a BRIEF explanation

d) Draw a reaction energy diagram with properly labelled axes that includes the activation energy for reaction in EACH DIRECTION and a drawing of the transition state, clearly indicates the positions on the diagram of both sets of reactants and the transition state
Question 4: Provide the missing major organic products or reagents/conditions for the following reactions. Assign each reaction as addition, rearrangement, substitution or elimination. Include all non-bonding electrons in the organic structures. Pay attention to relative stereochemistry as appropriate.

a) \[
\begin{align*}
\text{1. BH}_3\cdot\text{THF} & \\
\text{2. H}_2\text{O}_2, \text{OH} & \\
\end{align*}
\]

b) \[
\begin{align*}
\text{CH}_3 & \\
\rightarrow & \\
\text{CH}_3 & \text{OCH}_3
\end{align*}
\]

c) \[
\begin{align*}
\text{HBr} & \\
\rightarrow & \\
\text{ROOR} & \\
\end{align*}
\]

d) \[
\begin{align*}
\text{H}_2\text{O (solvent)} & \\
\rightarrow & \\
\text{H}_2\text{SO}_4 \text{ (cat.)/heat} & \\
\end{align*}
\]
Question 5.

a) Give a full curved-arrow pushing mechanism for the reaction shown below. Clearly indicate the initiation and the propagation steps in the radical chain mechanism. Classify the reaction as addition, substitution, elimination or rearrangement.

\[
\text{CH}_2=CH\text{CH}_2\text{CH}_3 + \text{Br}_2 \xrightarrow{hv} \text{CH}_2=CH\text{CH}_2\text{CH}_2\text{Br}
\]

b) Give a brief explanation (in words, 2 sentences maximum) why the product shown above is the major product of the reaction (i.e. why is the Br no attached to a different carbon atom), you do not need to draw any mechanisms or energy diagrams, but you will need to mention the important intermediate and use the term "Hammond postulate".

The critical intermediate is a radical, the radical intermediate for the reaction shown is tertiary and the most stable radical that can be formed from this structure. The Hammond postulate says that the most stable intermediate will be formed fastest, hence the major product is as shown.

c) The mechanism is a chain reaction give at least THREE possible chain termination reactions
Question 1: Give the IUPAC name for the following structure.

![Structure Image]

Question 2. Provide a curved arrow pushing mechanism for the following reaction, indicate the Lewis acids/bases at each step as appropriate and whether they are Bronsted acids/bases. Draw the transition state for EACH STEP IN THE MECHANISM.

![Reaction Diagram]
Question 3: For the following two reactions:

a) Give the products (include all important resonance contributors) and indicate which are the Lewis acids/bases (LB/LA) and whether they are also Bronsted acids/bases (BA/BB).

b) Draw a reaction energy diagram that includes both reactions on the same diagram, clearly indicate which reaction is which and include the activation energies for both reactions.

c) Are the reactions exothermic or endothermic, which would be more exothermic or more endothermic, which would be faster? Give a brief explanation that includes the term "Hammond postulate".
Question 4: Provide the missing major organic products or reagents/conditions for the following reactions. Assign each reaction as addition, rearrangement, substitution or elimination. Include all non-bonding electrons in the organic structures. Pay attention to relative stereochemistry as appropriate.

a) \[
\begin{array}{c}
\text{H}_2 \\
Pd/C
\end{array}
\]

b) \[
\begin{array}{c}
\text{Br}_2 \\
\text{EtOH}
\end{array}
\]

c) \[
\begin{array}{c}
1. \text{BH}_3\text{.THF} \\
2. \text{NaOH/H}_2\text{O}_2
\end{array}
\]

d) \[
\begin{array}{c}

\end{array}
\]
Question 5: Provided are spectra for a compound with molecular formula C₉H₁₂O, determine the structure by answering the questions below

a) Give the degrees of unsaturation ________________

b) On the infrared spectrum, indicate the peaks that identify the functional groups in the molecule (including C(sp³)-H). Indicate BOTH the functional group, and where appropriate, the specific BOND in the functional that corresponds to the peak.

(c) draw the structure and clearly indicate which hydrogens correspond to which signals in the proton nmr spectrum ONLY
Question 1. Give the IUPAC name for the following structure.

[Diagram of a molecular structure with a bromine substituent]

Question 2.

a) The critical step in photochemical bromination is endothermic reaction of an organic structure with a bromine atom to generate a radical and H-Br. For each of the following structures, decide which hydrogen atom would react with a bromine atom the fastest, add that hydrogen atom to the provided line-angle structures, give the curved arrow-pushing for reaction with a bromine atom and give the radical product (include resonance contributors as appropriate).

A

\[
\begin{align*}
\text{H} & \quad \longrightarrow \\
\text{Br} &
\end{align*}
\]

B

\[
\begin{align*}
\text{H} & \quad \longrightarrow \\
\text{Br} &
\end{align*}
\]

C

\[
\begin{align*}
\text{H} & \quad \longrightarrow \\
\text{Br} &
\end{align*}
\]

b) Rank the reactions in order of increasing rate, give an explanation that includes the term "Hammond postulate".

\[\text{slowest} \quad < \quad \text{____} \quad < \quad \text{____} \quad \text{fastest}\]
Question 5: Provide the missing major organic products or reagents/conditions for the following reactions. Assign each reaction as addition, rearrangement, substitution or elimination. Include all non-bonding electrons in the organic structures. Pay attention to relative stereochemistry as appropriate.

a) \[
\text{Br}_2 \quad \text{MeOH}
\]

b) \[
\text{NBS} \quad \text{hv}
\]

c) \[
\text{Br}^+ \quad \text{Br}^-
\]

d) \[
\text{HBr} \quad \text{CCl}_4
\]
Question 6. Which of the following two reactions would have the most negative enthalpy of reaction, give a BRIEF explanation that includes the a short discussion of the relevant factors that control electron energies. Classify the reactions as addition, rearrangement, substitution or elimination.

A  \[ \text{H}_2 \text{Pd/C} \rightarrow \]  
B  \[ \text{H}_2 \text{Pd/C} \rightarrow \]