Interaction Energies, kcal/mol

<table>
<thead>
<tr>
<th>Eclipsing</th>
<th>Gauche</th>
</tr>
</thead>
<tbody>
<tr>
<td>H/H</td>
<td>~1.0</td>
</tr>
<tr>
<td>He/Me</td>
<td>~1.4</td>
</tr>
<tr>
<td>H/Me</td>
<td>~2.6</td>
</tr>
<tr>
<td>He/Me</td>
<td>~1.1</td>
</tr>
<tr>
<td>He/Et</td>
<td>~2.9</td>
</tr>
<tr>
<td>t-Bu/Me</td>
<td>~2.7</td>
</tr>
<tr>
<td>Me/Me</td>
<td>~0.9</td>
</tr>
<tr>
<td>Et/Me</td>
<td>~0.95</td>
</tr>
<tr>
<td>i-Pr/Me</td>
<td>~1.1</td>
</tr>
<tr>
<td>t-Bu/Me</td>
<td>~2.7</td>
</tr>
</tbody>
</table>

Infrared Correlation Chart

- **3000–3100 cm\(^{-1}\)**: broad ~3000, 2 peaks
- **2850–2960 cm\(^{-1}\)**: broad ~3300
- **1600–1660 cm\(^{-1}\)**: small range, strong
- **1260–1400 cm\(^{-1}\)**: range of values, broad peak

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

- **3-5 Hz**: small range, strong
- **7-10 Hz**: range of values, broad peak

NMR Correlation Charts

- **Amide (CO)\(\_\_\)NH**
- **Aromatic (Ar-H)** mainly 8 - 6.5 Hz
- **Alkyl (\(\_\_\)CH\(\_\_\))**
- **Alkyl (\(\_\_\)CH\(\_\_\)NR\(\_\_\))**
- **Alkyl (\(\_\_\)CH\(\_\_\)C\(\_\_\)C\(\_\_\)NR\(\_\_\))**
- **Aromatic (Ar-\(\_\_\)C=CR\(\_\_\))**
- **Aromatic (Ar-\(\_\_\)C=CR\(\_\_\))**
- **Aromatic (Ar-\(\_\_\)C=CR\(\_\_\))**

Extra Credit: _______/5
Total (incl Extra): _______/175+5
There is no need to ask Dr. Gould or any of the TAs, there is NO NOMENCLATURE problem on this test!

Question 1 (20 pts.) Show how you would make the target compound on the right from the starting compound on the left. Show reagents and conditions where appropriate, and the structures of important intermediate compounds. Do not show any (arrow pushing) mechanisms. Ignore stereochemistry.

Extra Credit Question (5 pts.) In which kind of biomolecule can a photochemical 2 + 2 cycloaddition reaction take place

- DNA
- phospholipid
- carbohydrate
- protein
Question 2 (36 pts)  Give the major organic products of the following reactions, indicate the stereochemistry using wedged/dashed bonds as appropriate and be sure to indicate the presence of any racemic mixtures. **State whether a solution of the product(s) would be optically active or not, with a very brief explanation.**

a) \[
\text{Na}^+ \cdot \text{OEt} \quad \text{EtOH} \rightarrow \quad \text{optically active single enantiomer}
\]

b) \[
1 \text{ Equiv. HCl} \rightarrow \quad \text{NOT optically active racemic mixture}
\]

c) \[
\text{NOT optically active racemic mixture}
\]

d) \[
\text{NOT optically active achiral}
\]

Question 3 (18 pts)  Draw the structures of the alcohol, the deprotonated alcohol and alkyl halide in the appropriate boxes you would use to complete the best Williamson ether synthesis of the provided ether, and fill in the base reagent required to deprotonate the alcohol.
Question 4 (38 pts.) For the following reaction, give a full curved-arrow pushing mechanism for formation of products A and B. **Indicate the Lewis acid and base at each step (LA or LB) and whether they are also Bronsted acids and bases (BA or BB). Include all reasonable resonance contributors for any intermediates AND INDICATE THE MAJOR RESONANCE CONTRIBUTOR as APPROPRIATE!**

b) Indicate which product, A or B, would be formed under thermodynamically controlled conditions and which would be formed under kinetically controlled conditions and give a BRIEF explanation of the role of temperature in determining kinetic and thermodynamic control

kinetic = A, thermodynamic = B, B is more likely to be formed at HIGH temperature since higher temperature enables REVERSIBLE reactions and allows the reaction to explore the entire reaction energy surface and find the lowest energy product, at low temperatures the reactions are irreversible and the fastest formed product is the major product

c) Draw an energy diagram for formation of both A and B ON THE SAME DIAGRAM, clearly indicate which curve refers to formation of A and which to formation of B.
Question 5 (21 pts.) In the provided structure, identify THREE carbon-carbon bonds that can be made using a Grignard reaction, give the structures of the Grignard and the molecule that it reacts with, acid workup steps (H$_3$O$^+$) are assumed you do not need to include them. CLEARLY indicate the C-C bond you are making in each reaction with an arrow.

\[
\begin{align*}
\text{MgBr} & \quad + \quad \text{HCO}_2 & \quad \rightarrow \quad \text{Me} \quad - \quad \text{MgBr} \\
\text{Me} & \quad + \quad \text{Me} & \quad \rightarrow \quad \text{Me} \\
\text{Me} & \quad + \quad \text{BrMg} & \quad \rightarrow \quad \text{Me} \\
\end{align*}
\]

Question 6 (18 pts) For the following electrocyclic ring closure reaction

\[
\begin{align*}
\text{heat} & \quad \rightarrow \\
\text{F}_3\text{C} & \quad \text{CF}_3 \\
\end{align*}
\]

a) give the curved arrow-pushing that describes the bond-making and bond breaking

b) on TOP of the reactant, draw a representation of the wavefunction of the HOMO using the approximate "p A.O." method (assume that the structure is slightly tilted so that you can see the phases of the orbital)

c) does the allowed reaction proceed via a conrotatory or disrotatory ring closure? 

\underline{\text{disrotatory}}
Question 7 (24 pts). Give the ALLOWED product of the following cycloaddition reaction:

\[ \text{Product: cis-cycloaddition} \]

a) Give the curved arrow-pushing that describes the bond-making and breaking.

b) Redraw the cation A and give a pictorial representation of the wavefunction of the HOMO ON TOP OF THE STRUCTURE.

c) Redraw the dicyanoethylene B and give a pictorial representation of the wavefunction of the LUMO ON TOP OF THE STRUCTURE.

d) Is the allowed reaction suprafacial/suprafacial or suprafacial/antarafacial, give a brief explanation based on your drawings of the molecular orbitals, you MUST include the following terms: HOMO, LUMO, transition state.

- The ALLOWED product of the reaction must have two bonding interactions in the transition state, consideration of the wavefunctions of the HOMO and the LUMO indicates that suprafacial/suprafacial reaction is allowed, thus the 2-CN groups start cis- and are on the same side in the product, and the two Me-groups on the outside of the cation end on the same side in the product.

e) Indicate ALL of the chiral/asymmetric centers in the product of the reaction using the * symbol, and explain whether a solution of the product would be optically active or not and why or why not not optically active, MESO compound.