H/Eclipsing/H ~1.0

Eclipsing/H/Me ~1.4

Me/Me ~2.6

Me/Me ~0.9

Et/Me ~0.95

i-Pr/Me ~1.1

t-Bu/Me ~2.7

Gauche/Et/Me ~2.9

Interaction Energies, kcal/mol

<table>
<thead>
<tr>
<th>Interaction</th>
<th>Eclipsing</th>
<th>Gauche</th>
</tr>
</thead>
<tbody>
<tr>
<td>H/H</td>
<td>-1.0</td>
<td>Me/Me</td>
</tr>
<tr>
<td>H/Me</td>
<td>-1.4</td>
<td>Et/Me</td>
</tr>
<tr>
<td>Me/Me</td>
<td>-2.6</td>
<td>i-Pr/Me</td>
</tr>
<tr>
<td>Et/Me</td>
<td>-2.9</td>
<td>t-Bu/Me</td>
</tr>
<tr>
<td>Et/Et</td>
<td>-3.1</td>
<td></td>
</tr>
</tbody>
</table>

Infrared Correlation Chart

- C–H: 3000–3100 cm⁻¹
- N–H: 3300 cm⁻¹, broad with spikes ~3300
- O–H: 3300 cm⁻¹, broad
- C=O: 2500 cm⁻¹, usually strong
- C=N: 2200 cm⁻¹
- C≡N: 2200 cm⁻¹
- C≡CH: 2200 cm⁻¹
- C=O: 1735 cm⁻¹
- O–H: 3300 cm⁻¹, broad
- O–C–O: 1650 cm⁻¹, 1500 cm⁻¹

Points by question

1__________/15
2__________/22
3__________/36
4__________/16
5__________/32
6__________/12
7__________/90
8__________/20
Extra Credit_____/5
9__________/44
Total ____/175+5
(incl Extra)
10__________/44
11__________/44

* MOLECULAR MODELS ARE ALLOWED *

**YOU ARE NOT ALLOWED TO KEEP SPARE COPIES OF THIS EXAM **
Question 1 (15 pts.) Provide a IUPAC name for the following structure, do not forget to use E/Z and R/S as appropriate.

\[
\text{(4S)-bromo-4-cyclohexylbutanoic acid}
\]

Question 2 (22 pts.) Serum creatinine levels in humans are used to measure renal function. Creatinin exists in several tautomeric forms, two are shown below.

Write a curved arrow-pushing mechanism that shows how the structure on the left is converted into the one on the right. *Hint: this is essentially the same as acid catalyzed ketone to enol tautomerization.*

**Show where all protons come from and go to (no +H^+/-H^-)**
**Show all resonance contributors to the intermediate structures**
**Label the Lewis acid/base and and Bronsted acids/bases as appropriate**

Extra Credit Question (5 pts). Tartaric acid has historical significance in the discovery of which phenomenon in organic chemistry?

NMR spectroscopy       **chirality**       polymerization       aromaticity
Question 3 (36 pts.) On each side of the following equilibrium:

a) add the curved arrow pushing in both directions
b) add any missing resonance contributors for the two base anions
c) identify the stronger and weaker acid and base on each side
d) indicate which acid would have the LOWER pKa
e) Give a properly labelled reaction energy diagram with a drawing of the transition state
f) Give a brief explanation for your choices of strong and weak acids and bases that includes the term “energy of the electrons”.
g) Which is the stronger Bronsted acid, an ester or an amide? __________

the stronger base has higher energy electrons because the nitrogen acts as a stronger donating group compared to the weaker oxygen donating group on the weaker base

Question 4 (16 pts.) Give a curved arrow-pushing mechanism for the following two reactions
• SHOW WHERE EVERY PROTON COMES FROM AND GOES TO
• Indicate the Lewis acid and base (LA or LB) at each INTERMOLECULAR step and whether they are also Brønsted acids and bases (LA/BA or BA/BB)
Question 5 (32 pts)
• Give a curved arrow pushing mechanism for the following acid catalyzed Aldol reaction
• For each INTERMOLECULAR step, indicate the Lewis acid and base (LA or LB) and whether they are also Bronsted acids and bases (BA or BB) as appropriate
• You MUST show where every proton comes from and goes to, no abbreviated +H⁺/-H⁺ notation you do NOT need to show resonance contributors for the intermediates in this case!

Question 6 (12 pts) Which of the following two structures below, A or B, is the strongest Bronsted base? Give a brief explanation that includes the term “energy of the electrons”.

B is the strongest base, it has higher energy electrons, in both cases the negative charge is stabilized by resonance but in A it is delocalized onto the electronegative oxygen
Question 7 (90 pts) Provide the missing major organic products or reagents/conditions for the following reactions. Unless otherwise indicated, do not forget to include stereochemistry as appropriate and indicate any racemic mixtures.

a) \( \text{heat} \)

\[
\text{MMA} + \text{CH}_3\text{CO}_2\text{CH}_3 \rightarrow (\pm) \text{product}
\]

b) \( 	ext{H}^+ \text{cat.} \)

\[
\text{HCO} \rightarrow (\pm) \text{product}
\]

c) \( \text{1. NaCN} \), \( \text{2. LiAlH}_4 \), \( \text{3. H}_3\text{O}^+ \)

\[
\text{MgBr} + \text{phenyl} \rightarrow (\pm) \text{product}
\]

d) \( \text{NaBH}_4/\text{EtOH} \)

\[
\text{Cyclic ketone} \rightarrow \text{HO-alkyl}
\]

(ignoring stereochemistry)

e) \( 1. \text{NaCN} \), \( 2. \text{LiAlH}_4 \), \( 3. \text{H}_3\text{O}^+ \)

\[
\text{MgBr-alkyl} \rightarrow \text{bis-phenyl}
\]

f) \( \text{1. Ph-MgBr} \), \( \text{2. H}_3\text{O}^+ \)

\[
\text{Ester} \rightarrow \text{Ph-alkyl}
\]
Question 7, Contd... Provide the missing major organic products or reagents/conditions for the following reactions. **Unless indicated otherwise, do not forget to include stereochemistry as appropriate** and **INDICATE ANY RACEMIC MIXTURES.**

- **h)**
  
  ![Chemical structure](image)
  
  Reaction:
  
  1 Equiv. CH₃NH₂
  
  1 Equiv. CH₃NH₂
  
  **ignore stereochemistry**

- **i)**
  
  ![Chemical structure](image)
  
  Reaction:
  
  1 LiAlH₄
  
  2. H₃O⁺

- **j)**
  
  ![Chemical structure](image)
  
  Reaction:
  
  HCl (cat.)
  
  Heat

- **k)**
  
  ![Chemical structure](image)
  
  Reaction:
  
  1. Na⁺-OEt
  
  2. H₃O⁺

**Question 8 (20 pts)** Give all reactants/reagents and conditions that would be used to give the provided structures in the Claisen and Aldol reactions below. Ignore stereochemistry for these problems.

- **i)**
  
  ![Chemical structure](image)
  
  Reaction:
  
  1 LiAlH₄
  
  2. H₃O⁺

- **k)**
  
  ![Chemical structure](image)
  
  Reaction:
  
  1. Na⁺-OMe/MeOH
  
  2. H₃O⁺
**Question 9** (44 pts.) Show how you would make the target compounds on the right from the starting compounds on the left. Show reagents and conditions where appropriate, and the structures of important intermediate compounds. Do not show any (arrow pushing) mechanisms. **If necessary, you must indicate steps that require separation of isomers**
Question 10 (44 pts.) Give a curved arrow-pushing mechanism for the following reaction. Show where all protons come from and go to (no $\text{H}^+$/H$^-$). Show all resonance contributors to the intermediate structures. Label the Lewis acid/base and Bronsted acids/bases as appropriate.

a) 

\[
\begin{align*}
\text{LB} \quad \text{NH}_2 \quad + \quad \text{LA} \quad \xrightarrow{\text{heat}} \quad \text{acetaminophen - painkiller} \\
\text{LB/BB} \\
\text{LA/BA}
\end{align*}
\]

b) 

\[
\begin{align*}
\text{LB/BB} \quad \xrightarrow{\text{LA/BA}} \quad \xrightarrow{\text{H}_3\text{O}^+} \quad \text{LA/BA} \quad \xrightarrow{\text{heat}} \quad \text{LB/BB} \\
\text{LB} \\
\text{LA/BA} \\
\text{LB/BB}
\end{align*}
\]

acetaminophen - painkiller
Question 11 (44 pts.) Synthesize the (target) molecule on the right from the starting molecule the left. This cannot be done in one reaction. Give reagents and conditions and the intermediate molecules at each step. Do not show any mechanisms or transient intermediates. 

Ignore stereochemistry!

**a)**

1. **KMnO$_4$/OH/H$_2$O**
2. $\text{H}_3\text{O}^+$

**NBS/h$_\nu$**

**1. LiAlH$_4$/H$_2$/Pd/C**
2. $\text{H}_3\text{O}^+$

**PCC**

**SOCl$_2$**

**Br$_2$/h$_\nu$ or...**

**NBS/h$_\nu$**

**b)**

**Br**

**Mg . THF**

1. CO$_2$
2. $\text{H}_3\text{O}^+$

**SOCl$_2$**

**H$_2$C$_2$O**

**HO$_\text{C}_2$H**