**YOU ARE NOT ALLOWED TO TAKE SPARE COPIES OF THIS EXAM FROM THE TESTING ROOM**

- PRINT YOUR NAME ON EACH PAGE!
- READ THE DIRECTIONS CAREFULLY!
- USE BLANK PAGES AS SCRATCH PAPER
  work on blank pages will not be graded...
- WRITE CLEARLY!
- MOLECULAR MODELS ARE ALLOWED
- DO NOT USE RED INK
- DON'T CHEAT, USE COMMON SENSE!

**Infrared Correlation Chart**

<table>
<thead>
<tr>
<th>Interaction Energies, kcal/mol</th>
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<tbody>
<tr>
<td><strong>Eclipsing</strong></td>
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<tr>
<td>H/H ~1.0</td>
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<tr>
<td>Me/Me ~0.9</td>
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<tr>
<td>Me/Me ~2.6</td>
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<tr>
<td>Et/Me ~3.1</td>
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<tr>
<td>i-Pr/Me ~1.1</td>
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<tr>
<td>t-Bu/Me ~2.7</td>
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<tr>
<td><strong>Gauche</strong></td>
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<td>H/Me ~1.4</td>
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<tr>
<td>Me/Me ~0.95</td>
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<tr>
<td>Me/Me ~2.6</td>
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<tr>
<td>Et/Er ~3.1</td>
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</tbody>
</table>

**NMR Correlation Charts**

- O - H: 3300
- C = O: usually strong
- N - H: broad with spikes ~3300
- C = C - CH: 2200
- C = CH: 2200
- C = C - CH: 2200
- O - C - O: broad ~3000
- N - H: 3300
- R - NH₂: variable and condition dependent, ca. 2-6 δ
- R - OH: (δ, ppm)
- Aromatic: Ar - H: mainly 8-6.5
- Alkyl: 3' > 2' > 1'
- Alky: 3' > 2' > 1'
- R - C - OH: 11 10 9 8 7 6 5 4 3 2 1 0
- R - C - OH: 220 200 180 160 140 120 100 80 60 40 20 0
- R - C - OH: N - H: 3000-3100
- C = O: 2720-2820 2 peaks
- C = C - CH: 2200
- C = CH: 2200
- C = C - CH: 2200
- O - C - O: broad ~3000

The room where most students will take the test for your class, i.e. LS A-191 for onground and PS H-152 for hybrid.)
YOU MUST COMPLETE THIS PAGE WITH YOUR NAME
(EVEN THOUGH YOU ALREADY DID THIS ON THE COVER PAGE)
AND ALSO GIVE YOUR ASU OR POSTING ID NUMBER
we need this information because we will not be able to read the names of many students!

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Question 1 (13 pts.) Provide an IUPAC name for the following structure, do not forget to use E/Z and R/S as appropriate.

5-bromo-(2S)-phenylpentanoic acid

Question 2 (14 pts.) Give TWO reasons why an acid chloride hydrolyzes to a carboxylic acid in pure water at room temperature, but an amide requires strong acid or base catalysis and heat.

The reaction involves nucleophilic addition to the C=O bond, the amide has a donating group attached to this carbon, the chloride a withdrawing group, also the amide anion is a poor leaving group whereas chloride is a good leaving group.

Question 3 (16 pts) Using a drawing of a minor resonance contributor, explain why protonation occurs on nitrogen in reaction A, but on oxygen in reaction B.

The nitrogen is more basic in reaction A because the non-bonding electrons are on the less electronegative element and also in an sp3 hybridized orbital.

The resonance contributor shows a partial negative charge on oxygen in the structure in B and a partial positive charge on the nitrogen, reducing the basicity of the nitrogen and increasing the basicity of the oxygen.

Extra Credit Question (5 pts). What kind of functional group is hydrolyzed to form soap?

- carboxylic acid
- ester
- amide
- aldehyde

- ester
Question 4 (20 pts.) Rank the following in order of increasing Bronsted acidity. Give a BRIEF explanation that includes drawings of the conjugate base anions, including ALL relevant resonance contributors.

Acidity is determined by the stability of the enolate anions formed by deprotonation of the indicated hydrogens.

- The anion for B is stabilized by 3 resonance contributors, it is the most stable base, its acid is the strongest.
- The anions for both A and C are stabilized by 2 resonance contributors, in C the anion is stabilized by the weak W group and in A the anion is destabilized by the donating group, A is the weakest acid.

Question 5 (8 pts.) Which would you expect to be the stronger Bronsted Base? Give a BRIEF explanation that includes the term "energy of electrons" and "chemical reactivity".

The non-bonding electrons in A are stabilized by resonance delocalization, the electrons are thus lower in energy and are thus less chemically reactive, A is the weaker Bronsted base.
Question 6 (34 pts) Give a curved arrow pushing mechanism for the following reactions

- AS APPROPRIATE, SHOW WHERE ALL PROTONS COMES FROM AND GO TO (no $+H^+/H^-$)
- DRAW ALL RESONANCE CONTRIBUTORS for the intermediates as appropriate
- At 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

(a) 

(b) 

\[ \text{La/BA} \quad \text{Na}^+ \text{-OH/H}_2\text{O} \quad \text{La/BA} \]
Question 7 (64 pts) Provide the missing major organic products or reagents/conditions for the following reactions. Do not forget to include stereochemistry as appropriate and INDICATE ANY RACEMIC MIXTURES.

a) 
\[
\begin{align*}
\text{Br} & \quad \xrightarrow{1. \text{NaCN}} \quad \text{NH}_2
\end{align*}
\]

b) 
\[
\begin{align*}
\text{HOC}_2\text{H}_3 + \text{C}_6\text{H}_5\text{OCH}_3 \quad & \quad \xrightarrow{1. \text{NaOMe/MeOH}} \quad \text{PhOOC}_2\text{H}_3 \quad (\pm)
\end{align*}
\]

c) 
\[
\begin{align*}
\text{heat} & \quad \xrightarrow{} \quad \text{CN}
\end{align*}
\]

d) 
\[
\begin{align*}
\text{Cl} & \quad \xrightarrow{1. \text{H-N}} \quad \text{N}
\end{align*}
\]

\textit{this requires more than one step}

e) 
\[
\begin{align*}
\text{Br} & \quad \xrightarrow{1. \text{Na}^+\text{-N}_3} \quad \text{OCH}_2\text{CH}_2\text{NH}_2
\end{align*}
\]

\textit{1. Excess LiAlH}_4 \quad \textit{3. H}_3\text{O}^+

f) 
\[
\begin{align*}
\text{NaBH}_4/\text{EtOH} & \quad \xrightarrow{} \quad \text{HO}
\end{align*}
\]

(\text{ignore stereochemistry})
Question 7, Contd... Provide the missing major organic products for the following reactions. Do not forget to include stereochemistry as appropriate and INDICATE ANY RACEMIC MIXTURES.

g) \[
\begin{align*}
\text{Ph} & \quad \text{H} \\
\text{O} & \quad \text{TsOH} \\
\text{heat} & \quad \text{Ph} \\
\text{H} & \quad \text{O} \\
\text{H} & \quad \text{C} \\
\text{MeOH} & \quad \text{or Z-isomer}
\end{align*}
\]

h) \[
\begin{align*}
\text{C} & \quad \text{O} \\
\text{Cl} & \quad \text{MeOH} \\
\end{align*}
\]

Question 8 (12 pts.) The following is a Stork enamine synthesis. There are 3 steps. Add the relevant reagents/conditions for each of the 3 steps.

\[
\begin{align*}
\text{HO} & \quad \text{O} \\
\text{N} & \quad / \text{H+ cat.} \\
\text{H} & \quad \text{3} \\
\text{O} & \quad + \\
\text{Br} & \quad \text{2. Br} \\
\text{H}_3\text{O}^+ & \quad \text{3. H}_3\text{O}^+ \\
\end{align*}
\]

(ignore stereochemistry)

Question 9 (10 pts.) Give the TWO organic products expected for the following Hoffman elimination

\[
\begin{align*}
\text{H} & \quad \text{N} \\
\text{I} & \quad \text{1. Excess MeI} \\
\text{2. Ag}_2\text{O}/\text{heat} \\
\end{align*}
\]
CheMistry 234, Spring 2017  FInal Exam

QuesTion 10 (22 pts)
a) Give the allowed product of the electrocyclic ring closure reaction shown below and give the
curved arrow-pushing describing bond making/breaking

\[ \Delta \]

\[ HOMO \]

b) How many electrons are involved in this reaction 6

c) Does the ALLOWED reaction proceed via a disrotatory or a conrotatory ring closure disrotatory

d) Does the allowed reaction proceed via a Huckel or a Mobius transition state? Give a BRIEF

explanation that includes the term "aromatic"

Huckel, because 6 electrons in a cyclic loop Huckel transition state are aromatic and lower in energy than a Mobius transition state

e) Draw the HOMO of the reactant anion ON TOP of the

structure to the right

QuesTion 11 (20 pts.) Give the arrow pushing mechanism for the following reaction. Show where
each proton goes to and comes from (no +H*/-H*), indicate the LB/BB and LA/BA, and show all
reasonable resonance contributors for the intermediates, add H atoms and non-bonding
electrons as necessary, and Clearly identify all enolate anions in your mechanism!

How many steps are in your mechanism? 5
Question 12 (18 pts)
a) Give the reactants AND reagents/conditions that would allow you to synthesize malonic ester in a Claisen reaction

\[
\begin{align*}
\text{EtO} & \quad \text{OEt} \\
\text{excess} & \quad \text{EtO} \\
\text{O} & \quad \text{O} \\
\text{OEt} & \quad \text{OEt} \\
\end{align*}
\]

1. Na\(^+\)\cdot\text{OEt} \\
2. H\(_3\)O\(^+\) \\

malonic ester

b) Give the reactants AND reagents/conditions that would allow you to synthesize cis-Jasmone (used in perfume industry) in an Aldol condensation.

any reasonable acid/base heat

cis-Jasmone

Question 13 (16 pts) Rank the following in order of increasing rate of electrophilic aromatic substitution, for example, reaction with Br\(_2\)/FeBr\(_3\). Provide a BRIEF explanation that includes the terms activating and deactivating.

\[
\begin{align*}
\text{A} & \quad \text{B} & \quad \text{C} \\
\end{align*}
\]

\[
\begin{align*}
\text{A} & \quad < \quad \text{B} & \quad < \quad \text{C} \\
\end{align*}
\]

electrophilic aromatic substitution is faster with stronger donating more activating substituents

the substituent in A is withdrawing and deactivating, it is slowest

the substituent in B is donating and activating, but the substituent in C is stronger donating and more activating, thus C is fastest
Question 14 (22 pts.) Give a curved arrow-pushing mechanism for the following reaction

- SHOW WHERE EVERY PROTON COMES FROM AND GOES TO (no +H\(^+\) or -H\(^-\))
- DO NOT DRAW RESONANCE STRUCTURES for the intermediates
- Add non-bonding electrons and C–H bonds as necessary
- Indicate the Lewis acid/bases (LA or LB) and Bronsted acids/bases (BA or BB) for each INTERMOLECULAR step

Assume the reaction is performed in an not very polar solvent where the H-Cl is NOT dissociated.
Question 15 (46 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. For question a) you must indicate steps that require separation of isomers and ALSO GIVE THE STRUCTURES OF THE OTHER ISOMER(S).

THE NEXT TWO SYNTHESIS PROBLEMS, b) and c), USE ONLY REACTIONS FROM THE "MINIMAL SET OF REACTIONS" PROVIDED RECENTLY ON THE CLASS WEB PAGE!

b) 

1. BH$_3$-THF
2. ROOR

Mg, THF

2. H$_3$O$^+$

(ignoring stereochemistry)

c) 

1. BH$_3$-THF
2. $\cdot$OH/H$_2$O$_2$

PCC

1. PhMgBr
2. H$_3$O$^+$
Question 16 (40 pts.) In each case, synthesize the (target) molecules on the right from the starting molecules 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.

a) (ignore stereochemistry)

\[
\begin{align*}
\text{Mg.THF} & \quad \quad \text{Br} \\
\text{HBr} & \quad \quad \text{OH} \\
\text{NaBH}_3 & \quad \quad \text{COCl} \\
\text{HNMe}_2 & \quad \quad \text{PCC} \\
\text{PCC} & \quad \quad \text{Mg.THF}
\end{align*}
\]

b) (ignore stereochemistry)

\[
\begin{align*}
\text{SOCl}_2 & \quad \quad \text{HNMe}_2 \\
\text{HNMe}_2 & \quad \quad \text{Br}
\end{align*}
\]