**INSTRUCTIONS**

- PRINT YOUR NAME ON EACH PAGE!
- READ THE DIRECTIONS CAREFULLY!
- USE BLANK PAGES AS SCRATCH PAPER
- WRITE CLEARLY!
- MOLECULAR MODELS ARE ALLOWED
- DON’T CHEAT, USE COMMON SENSE!

**INFRARED CORRELATION CHART**

- **C-H**
  - 3300 cm⁻¹
  - Usually strong
- **N-H**
  - Broad with spikes ~3300 cm⁻¹
  - Broad ~3300 cm⁻¹
- **O-H**
  - Broad ~3300 cm⁻¹

**NMR CORRELATION CHARTS**

- **R-NH₂**
  - Variable and condition dependent,
  - ca. 2 - 6 δ
- **R-OH**
  - Mainly 8 - 6.5
- **Aromatic**
  - Mostly 8 - 6.5
- **Alkyl**
  - 3° > 2° > 1°
- **Alkylic**
  - 3° > 2° > 1°
Question 1 (12 pts.) Provide an IUPAC name for the following structure, do not forget to use E/Z and R/S as appropriate.

a) ![Chemical structure][1]

7-bromo-(5S)-hydroxy-(6Z)-octenoic acid

OR

7-bromo-(5S)-hydroxyoct-(6Z)-enoic acid

Question 2 (20 pts.) Rank the following in order of increasing Bronsted acidity, and provide a BRIEF explanation. You MUST draw the structures of ALL OF the conjugate base anions including ALL reasonable resonance contributors.

A and B have 3 resonance contributors to the base anion, these are more stable than the base anion from C, therefore C is the weakest acid. In B the negative charge is delocalized onto 2 negatively charged oxygen atoms compared to an oxygen and a carbon for A, the anion from B is thus the most stable, B is thus the strongest acid.

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

- carboxylic acid
- ester
- amide
- aldehyde
Question 3 (20 pts.) For the following acid/base equilibrium:

a) draw the curved arrows showing bond making/breaking
b) indicate which is the STRONGER and the WEAKER acid and base on each side

c) give a BRIEF explanation for your choice of stronger/weaker that includes the phrase "energy of the electrons"

d) Indicate which reaction (left to right or right to left) is faster and which is slower and indicate on which side the equilibrium lies

e) Draw a PROPERLY labelled reaction energy diagram, indicate the position of the transition state and include a drawing of the transition state

\[ \text{N}H + \text{H}N \xleftrightarrow{\text{faster}} \text{N}H + \text{H} \]

\[ \text{stronger acid} \quad \text{stronger base} \quad \text{weaker acid} \quad \text{weaker base} \]

the energy of the electrons in the base on the right side are lower because the structure is aromatic, this is thus the weaker base and the weaker base has the stronger conjugate acid

d) Indicate which reaction (left to right or right to left) is faster and which is slower and indicate on which side the equilibrium lies

e) Draw a PROPERLY labelled reaction energy diagram, indicate the position of the transition state and include a drawing of the transition state

\[ \text{Energy} \quad \text{Reaction Coordinate} \]

Question 4 (10 pts.) Rank in order of increasing equilibrium constant for formation of a hydrate. Give a BRIEF explanation.

\[ \begin{array}{ccc}
\text{WD} & \text{WD} & \text{WD} \\
\text{A} & \text{B} & \text{C} \\
\text{WD} = \text{weakly donating} & \text{SD} = \text{strongly donating} \\
\text{smallest} & \text{smallest} & \text{largest}
\end{array} \]

this is addition of a weak nucleophile/LB, water, to a carbonyl C=O bond, which can be considered to be a small π-system, the carbonyl carbon in the ester B has a strong electron donating oxygen substituent on the carbonyl and a weak electrom donating methyl group, which decreases reactivity towards the LB/nucleophile, the ketone A has 2 weak alkyl donating substituents on the carbonyl carbon, the aldehyde C has only 1 weak alkyl donating group
Question 5. (20 pts.) Give a curved arrow-pushing mechanism for the reduction of the provided ester to butanol and methanol. You must draw the Lewis structure of the $\text{AlH}_4^-$ anion and you MUST show exactly where each proton comes from and goes to here, no $+\text{H}^+$ and $-\text{H}^+$ notation, and you must also show how the methanol is formed.

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1. LiAlH₄
2. H₃O⁺
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Question 6 (24 pts.) For the reaction between structures A and B below, you are going to determine whether the PROVIDED product is allowed or forbidden, using F.M.O. theory.

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

b) Was the PROVIDED PRODUCT (which may or may not be allowed) formed via suprafacial or antarafacial reaction for reactant A? suprafacial

c) Was the PROVIDED PRODUCT (which may or may not be allowed) formed via suprafacial or antarafacial reaction for reactant B? suprafacial

d) Draw the HOMO for A and the LUMO for B on TOP of the structures that are redrawn for you below, for EACH, give the number of vertical nodes

# vertical nodes = 0

HOMO for A

# vertical nodes = 1

LUMO for B

e) Is the cycloaddition reaction shown above allowed or forbidden. Give a BRIEF explanation that includes the words "suprafacial" and/or "antarafacial" as appropriate

forbidden, suprafacial/antarafacial reaction does not result in one bonding interaction and one ANTI-bonding interaction for the two new sigma bonds that need to be formed
Question 7 (72 pts) Provide the missing major organic products for the following reactions. Do not forget to include stereochemistry as appropriate and INDICATE ANY RACEMIC MIXTURES.

a) \[
\text{heat} \quad \overset{(\text{electrocyclic ring closure reaction})}{\rightarrow} \quad \text{product}
\]

b) \[
\begin{align*}
1. & \quad \text{Excess PhMgBr} \\
2. & \quad \text{H}_3\text{O}^+
\end{align*}
\]

c) \[
\begin{align*}
1. & \quad \text{Mg . THF} \\
2. & \quad \text{HNO}_3 \\
3. & \quad \text{H}_2\text{SO}_4
\end{align*}
\]

d) \[
\begin{align*}
1. & \quad \text{PhC}l \\
2. & \quad 1 \text{ equivalent}
\end{align*}
\]

e) \[
\begin{align*}
1. & \quad \text{Mg . THF} \\
2. & \quad \text{CO}_2 \\
3. & \quad \text{H}_3\text{O}^+
\end{align*}
\]

(f) \[
\begin{align*}
\text{heat} & \quad \overset{(\pm)}{\rightarrow} \quad \text{product}
\end{align*}
\]
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.

h)  
\[
\begin{align*}
\text{NH}_2 & \rightarrow 1. \text{Excess MeI} \\
& \rightarrow 2. \text{Ag}_2\text{O}/\text{heat} \\
\end{align*}
\]
(\text{ignore stereochemistry for this problem})

\[
\begin{align*}
\text{Ph} & \rightarrow \text{1. Na}^+\text{-OMe/MeOH} \\
& \rightarrow \text{2. H}_3\text{O}^+ \\
\end{align*}
\]
(\text{ignore stereochemistry for this problem})

i)  
\[
\begin{align*}
\text{Ph} & \rightarrow \text{1. Na}^+\text{-OMe/MeOH} \\
& \rightarrow \text{2. H}_3\text{O}^+ \\
\end{align*}
\]

j)  
\[
\begin{align*}
\text{Ph} & \rightarrow \text{TsOH cat. / heat} \\
\end{align*}
\]

Question 8 (8 pts) Give all reactants/reagents and conditions that would be used to give the provided structure below. Indicate whether the reaction is a Aldol reaction or a Claisen reaction.

\[
\begin{align*}
\text{OMe} & \rightarrow \text{1. Na}^+\text{-OMe/MeOH} \\
& \rightarrow \text{2. H}_3\text{O}^+ \\
\end{align*}
\]
(\text{ignore stereochemistry for this problem})

Question 9 (16 pts.) IN THE BOXES, give the missing reagents/conditions or structures, as required, to complete the following Stork (enamine) alkylation of cyclopentanone.
Question 10 (40 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.

These questions use only reactions from the "minimal" sets that were provided on the class website.

b)  

\[ \text{b) } \begin{align*} \text{HBr} & \rightarrow \text{Br} \\ \text{ROOR} & \rightarrow \text{Mg.THF} \\ \text{MgBr} & \rightarrow \text{OH} \end{align*} \]

(忽略立体化学)

Ph

Ph

MgBr

OH

Ph

Ph

MgBr

OH

Ph

Ph

H3O+

2.

OH

Ph

Ph

MgBr

OH

Ph

Ph

H3O+

1.

Ph

MgBr

OH

Ph

Ph

MgBr

OH

Ph

Ph

H3O+

1.

Ph

MgBr

OH

Ph

Ph

H3O+

2.

OH

Ph

Ph

MgBr

OH

Ph

Ph

H3O+

1.

OH

Ph

Ph

MgBr

OH

Ph

Ph

H3O+

2.
Question 11 (30 pts.) Give a curved arrow-pushing mechanism for the following reaction.
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 Bronsted acids/bases as appropriate.
Question 12 (35 pts). Give a curved arrow pushing mechanisms for the following two reactions.

1) Add non-bonding electrons and C-H bonds to the line-angle structures as required.
2) Indicate the Lewis acid/Lewis base (LA, LB) at each intermolecular step as appropriate, and whether they are also Brønsted acids/bases (LA/BA, LB/BB).
3) **YOU DO NOT HAVE TO DRAW RESONANCE CONTRIBUTORS** for intermediates.
4) **GIVE THE NUMBER OF STEPS IN YOUR MECHANISMS**
5) Show where ALL protons come from and go to, no abbreviated +H+/H+ notation.
Question 13 (40 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.

a)

\[
\begin{align*}
&\text{HO} \\
&\text{HO} \\
&\text{HO} \\
&\text{Br} \\
&\text{Na}^+\text{CN} \\
\end{align*}
\]

\[
\text{NBS / h} \\
\]

\[
\begin{align*}
&\text{HO} \\
&\text{HO} \\
&\text{HO} \\
&\text{CN} \\
&\text{dopamine} \\
\end{align*}
\]

b)

\[
\begin{align*}
&\text{HBr} \\
&\text{MgBr} \\
&\text{Mg.THF} \\
&\text{1. CO}_2 \\
&\text{CO}_2\text{H} \\
&\text{SOCl}_2 \\
&\text{MgBr} \\
&\text{Ph-NH}_2
\end{align*}
\]
Question 14 (20 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!

\[
\text{Br} \quad \xrightarrow{\text{Na}^+\text{CN}} \quad \xrightarrow{\text{SOCl}_2} \quad \text{CO}_2\text{H}
\]

Question 15 (8 pts.) Give the structure of the ketone and ALL OTHER reagents/conditions you would use to synthesize amphetamine via a reductive amination.

\[
\text{Ketone} \quad \xrightarrow{\text{NH}_2/\text{H}^+\text{ (cat.)}} \quad \xrightarrow{\text{H}_2/\text{Pd/C}} \quad \text{amphetamine}
\]