ORGANIC CHEMISTRY II (2302)

10:30 am – 12:30 pm, December 18, 2015

Final Exam

You will be able to pick up your graded exam from Chemistry department staff in 115 Smith beginning Tuesday, December 22\textsuperscript{nd} at 9 AM. Exams that are not picked up within two weeks will be disposed of.

Tables of amino acid and nucleic acid structures, a chart of reaction conditions, and a periodic table are attached to the back of this exam as an aid. Otherwise, you are not permitted to use any other materials (including notes, books, or electronic devices of any kind).

When the exam begins, please write your name at the top of the next page.

You may use pen or pencil. However, re-grades will be considered only for exams completed in pen.

Please write your answers in the boxes/spaces provided. If your answer is not in the appropriate space (say, for example, it’s on the back of the page), draw us an arrow and/or note telling us where to look.
1. (16 pts) For cyclopropenyl anion,
   - How many molecular orbitals describe the conjugated $\pi$-system?
   - Draw all of these molecular orbitals on the energy diagram below. Draw both the shapes of the orbitals (as viewed from the top) and their energies, and fill the orbitals with the appropriate number of electrons.

   *example of answer format (for C$_2$H$_4$):*

   $$\begin{array}{c}
   E \\
   \hline \\
   \text{non-bonding level} \\
   \hline \\
   \begin{array}{c}
   \text{H} \\
   \text{H} \\
   \text{H} \\
   \text{H} \\
   \text{H} \\
   \text{H} \\
   \text{H}
   \end{array} \\
   \text{cyclopropenyl anion}
   \end{array}$$

   *your answer:*

   $$\begin{array}{c}
   E \\
   \hline \\
   \text{non-bonding level} \\
   \hline \\
   \begin{array}{c}
   \text{H} \\
   \text{H} \\
   \text{H} \\
   \text{H} \\
   \text{H} \\
   \text{H} \\
   \text{H}
   \end{array} \\
   \text{cyclopropenyl anion}
   \end{array}$$

   - Is the ion **AROMATIC** or **ANTIAROMATIC**? (Circle one.)
2. (6 pts) For each of the following molecules, circle whether the molecule is aromatic, anti-aromatic, or neither.

AROMATIC

ANTI-AROMATIC

NEITHER

3. (52 pts) Each of the reactions below is drawn with two possible products. If one of the two products predominates, circle that preferred product. If the two products are produced equally, circle “BOTH”. If neither product would result from the reaction, circle “NEITHER”. **Circle one answer only.**

HBr, 40 °C

Δ

1. HO""OH

HCl

2. CH₃MgBr (excess)

3. H₃O⁺
1. Dissolve in a mixture of aqueous base (NaOH/H₂O) and CHCl₃.
2. Discard CHCl₃ layer.
3. Add fresh CHCl₃ and enough HCl to make the H₂O solution acidic.
4. Discard H₂O layer.
1. LDA, -78 °C, in THF
2. \(\text{Br}

\begin{align*}
\text{BOTH (equally)} & \quad \text{NEITHER} \\
\end{align*}

1. \((\text{CH}_3)_2\text{CuLi}\)
2. \(\text{H}_2\text{O}\)

\begin{align*}
\text{BOTH (equally)} & \quad \text{NEITHER} \\
\end{align*}

1. \(\text{NaNO}_2\)
2. \(\text{HCl}\)

\begin{align*}
\text{BOTH (equally)} & \quad \text{NEITHER} \\
\end{align*}

\begin{align*}
\text{NaOH} & \quad \Delta \\
\end{align*}

\begin{align*}
\text{BOTH (equally)} & \quad \text{NEITHER} \\
\end{align*}
4. (26 pts) For each of the reactions below, fill in the empty box corresponding to reactants or product. Give only one answer in each box. For reactions that you expect to yield multiple products, draw one major product. For reactions that yield multiple enantiomers, draw only one enantiomer in the box, and include the note “+ enantiomer”.

\[ \text{a diene} \quad + \quad \text{a dienophile} \]

\[ \Delta \quad \rightarrow \quad \text{(+ enantiomer)} \]
1. \[ \text{Cyclohexanone} \rightarrow \text{(DIBAL-H)} \]
2. \[ \text{H}_2\text{O} \]

\[ \text{CH}_3 \]
\[ \text{CH}_3 \]
\[ \text{CH}_3 \]

\[ \text{Cyclohexane-1,4-dione} \rightarrow \text{NaOH} \rightarrow \Delta \]

\[ \text{Ph}_3\text{P} \rightarrow \text{Ph}_3\text{P=O} \]
5. (27 pts)
a. For each of the polymer syntheses proposed below, draw the polymer product using bracket notation (“\([-\text{M}]-\)”). If there is a part of the polymer structure that isn’t known (e.g., the initiating or terminating group), draw this as a squiggle in your structure.

1. DCC

2. (Grubbs’ catalyst)

\[
\text{H}_3\text{C} - \text{C} - \text{O} - \text{OH} \quad 1. \quad \text{CH}_3\text{OH} \quad \text{acrylonitrile} \quad 2. \quad \text{CH}_3\text{OH}
\]
b. If the second polymerization above were initiated with benzyol peroxide instead of with an anion, the mechanism of polymerization would be different. In the box below, add \textbf{curved arrows} (using “electron pushing”) that show how benzyol radical would initiate polymerization. Then draw the product of this step.

\begin{center}
\textbf{benzoyl initiation step: add curved arrows & step product}
\end{center}

\begin{center}
\text{benzoyl peroxide} \rightarrow \text{\begin{tikzpicture}
\draw[thick] (-0.5,0) -- (0.5,0);
\draw[thick] (0,-0.5) -- (0,0.5);
\draw[thick] (-0.5,0) -- (0,-0.5);
\draw[thick] (0.5,0) -- (0,0.5);
\draw[thick] (0,0) circle (0.2cm);
\end{tikzpicture}} \rightarrow \text{CN} \rightarrow \text{\begin{tikzpicture}
\draw[thick] (-0.5,0) -- (0.5,0);
\draw[thick] (0,-0.5) -- (0,0.5);
\draw[thick] (-0.5,0) -- (0,-0.5);
\draw[thick] (0.5,0) -- (0,0.5);
\draw[thick] (0,0) circle (0.2cm);
\end{tikzpicture}} \rightarrow \text{poly(acrylonitrile) B}"
\end{center}

c. How would you expect the molecular weight distribution (or “polydispersity”, measured by $PDI$) of the poly(acrylonitrile) polymers A and B described on this and the previous page to compare? Would you expect $PDI(\text{polymer A}) >$, $<$, or $=$ $PDI(\text{polymer B})$?

*(Circle one answer.)*

d. How would you synthesize a \textbf{co-polymer} of acrylonitrile and isoprene (the monomer shown at right)? Draw a synthetic recipe for the copolymer in the box below.

\begin{center}
\text{isoprene}
\end{center}

\begin{center}
\text{a copolymer of acrylonitrile and isoprene}
\end{center}

e. In two words or less, how would you convert your copolymer from a plastic into an elastomer?
6. (6 pts) D-Galactose, a common aldohexose found in nature, is the C-4 epimer of D-glucose. A Fischer projection of acyclic D-galactose is shown below.

a. Acyclic D-galactose equilibrates with a cyclic, 6-membered-ring (pyranose) form. Draw the structure of the β-anomer of this cyclic galactose as a Haworth projection in the box at right.

b. D-Galactose is combined in nature with D-glucose to form lactose, a disaccharide. Lactose is a glycoside of galactose. Which -OH group in your structure above would be replaced to form a glycoside? **Circle one -OH group.**

7. (29 pts) **Draw a mechanism** (using “electron pushing”) for each of the reactions shown on the next two pages. Draw each mechanistic step explicitly; don’t cheat by combining multiple processes in a single step, or by taking shortcuts. Use only the molecules shown in the problem.

Mechanism:
Mechanism:

RNA (B = a heterocyclic base)
8. (28 pts) Each of the syntheses shown below can be accomplished in just a few steps. For each starting material or set of starting materials, propose a multistep synthesis of the product shown. You may use any reagents and reactions we’ve learned about in class and/or in the text.

Do not use any reagents in excess.
9. (10 pts)
   a. Sort the three amino acids histidine (His), glutamic acid (Glu), and valine (Val) in order of increasing isoelectric point (pI). Write their three-letter abbreviations in the appropriate boxes below.

   histidine (His)
   glutamic acid (Glu)
   valine (Val)

   lowest pl
   H2N—COOH
   H2N—COOH
   H2N—COOH
   highest pl

   b. When valine is used in solid-phase peptide synthesis, it typically bears a tert-butyloxycarbonyl (tBoc) protecting group. In the box at right, draw the structure of tBoc-protected valine.
# Final Exam Chart of Reaction Conditions

<table>
<thead>
<tr>
<th>Condition</th>
<th>Reagent(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Br}_2$, $\text{FeBr}_3$</td>
<td>$\text{Cl}_2$, $\text{AlCl}_3$, $\text{H}_2\text{SO}_4$, $\text{HNO}_3$, $\text{Sn or Fe}$, $\text{HCl/H}_2\text{O}$</td>
</tr>
<tr>
<td>$1. \text{NaNO}_2$, $\text{HCl}$</td>
<td>$\text{R-X}$ ($R = \text{alkyl}$), $\text{AlCl}_3$ or $\text{FeBr}_3$</td>
</tr>
<tr>
<td>$2. \text{CuCN or H}_3\text{PO}_2$ or $\text{CuX or H}_3\text{O}^+$</td>
<td>$1. \text{N}_2\text{H}_4$, $\Delta$</td>
</tr>
<tr>
<td>$\text{Na}_2\text{Cr}_2\text{O}_7$, $\text{H}_2\text{SO}_4$, $\text{Bu}_4\text{N}^+\text{F}^-$</td>
<td>$\text{HO-}$</td>
</tr>
<tr>
<td>$\text{NaNH}_2$, $\text{Na}_2\text{H}_2\text{O}$, $\text{PhCH}_2\text{Br}$, $\text{Ag}_2\text{O}$, $\text{LiAlH}_4$, $\text{H}_2\text{O}$</td>
<td>$1. \text{LiAlH}_4$, $\text{H}_2\text{O}$</td>
</tr>
<tr>
<td>$\text{CHCl}_3$, $\text{KOrBu}$, $\text{CH}_2\text{I}_2$, $\text{Zn(Cu)}$, $\text{Pd(PPh}_3)_4$, $\text{NaOH}$, $\text{Zn(Cu)}$, $\text{LiOH}$</td>
<td>$\text{PPh}_3$, $\text{LDA}$</td>
</tr>
<tr>
<td>$\text{(Grubbs catalyst)}$</td>
<td>$\text{(DIBAL-H)}$, $\text{(CH}_3\text{)}_3\text{SiCl} {\text{TMSCl}}, \text{or TBDMSCl}$; $\text{Et}_3\text{N}$ or imidazole</td>
</tr>
<tr>
<td>$\text{ON}$</td>
<td>$\text{N}\equiv\text{C} \equiv\text{N}$</td>
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</tbody>
</table>

---

<table>
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<th>Reaction</th>
<th>Reagent(s)</th>
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<tr>
<td>$\text{Cl}/\text{Ru}/\text{PCy}_3$</td>
<td>$\text{CH}_2\text{I}_2$, $\text{Zn(Cu)}$, $\text{Pd(PPh}_3)_4$, $\text{NaOH}$, $\text{Zn(Cu)}$, $\text{LiOH}$</td>
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<td>$(\text{Grubbs catalyst})$</td>
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<td>$\text{L}/\text{Ph}$</td>
<td>$\text{H}_3\text{C}-\text{CH}_3$, $\text{H}_3\text{C}-\text{CH}_3$, $\text{AIBN}$</td>
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<td>$\text{PCy}_3$</td>
<td>$\text{CH}_2\text{I}_2$, $\text{Zn(Cu)}$, $\text{Pd(PPh}_3)_4$, $\text{NaOH}$, $\text{Zn(Cu)}$, $\text{LiOH}$</td>
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</tbody>
</table>
Final Exam Chart of Amino Acids
(in Alphabetical Order)

- Alanine (Ala, A)
- Arginine (Arg, R)
- Asparagine (Asn, N)
- Aspartic acid (Asp, D)
- Cysteine (Cys, C)
- Glutamic acid (Glu, E)
- Glutamine (Gln, Q)
- Histidine (His, H)
- Isoleucine (Ile, I)
- Leucine (Leu, L)
- Lysine (Lys, K)
- Methionine (Met, M)
- Phenylalanine (Phe, F)
- Proline (Pro, P)
- Serine (Ser, S)
- Threonine (Thr, T)
- Tryptophan (Trp, W)
- Tyrosine (Tyr, Y)
- Valine (Val, V)
Final Exam Chart of Nucleic Acid Bases (in Alphabetical Order)

- Adenine (A)
- Cytosine (C)
- Guanine (G)
- Thymine (T)
- Uracil (U)
**Periodic Table of the Elements**

<table>
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<th>Group</th>
<th>Element</th>
<th>Symbol</th>
<th>Atomic Number</th>
<th>Average Atomic Mass</th>
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**Key**
- Atomic number
- Element symbol
- Element name
- Average atomic mass

* If this number is in parentheses, then it refers to the atomic mass of the most stable isotope.

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