Chemistry 341

Final Exam
December 20, 2000

Dr. McMahon

This exam consists of 15 questions on 13 pages. Various tables of information are provided in a separate handout.

Print Name ____________________________

Grading key

Circle your TA's name

Wendy deProphetis
Melissa Feenstra
Gina Gencarelli
Lisa Jungbauer
Sarah Maifeld
Meg Schmitt
John Stevens

Circle the day and time of your Discussion Session

Tue 3:30 pm
  4:35 pm
  5:40 pm

Wed 3:30 pm
  4:35 pm

Total ______ / 150

Grading
1. ______ / 14
2. ______ / 9
3. ______ / 6
4. ______ / 9
5. ______ / 12
6. ______ / 9
7. ______ / 21
8. ______ / 10
9. ______ / 4
10. ______ / 4
11. ______ / 10
12. ______ / 12
13. ______ / 6
14. ______ / 12
15. ______ / 12
1. There are four D-aldopentose sugars (see Figure 16.1 in your information packet). On reduction with NaBH₄, two of these D-aldopentoses give the same alditol.

(a) Draw the structure and give the name of the two D-aldopentose starting materials, draw the structure of the alditol product, and specify whether or not the alditol is chiral.

(b) Draw the alditol products derived from the other two D-aldopentose isomers, and specify whether or not each product is chiral.
(9 pts) 2. Draw a structural formula for the following tripeptide (see Table 17.1 in your information packet). Mark each peptide bond, N-terminal amino acid, and C-terminal amino acid.

Phe-Val-Asn

(6 pts) 3. (a) In the following nucleoside, circle the anomeric carbon.

No credit if they circle the correct anomeric carbon along with other carbons

(b) One strand of DNA has the following sequence of bases: 5' GTACCGTT 3'. What is the sequence of bases on the complementary strand? Circle the letter of the correct answer.

i) 3' TGCAGCTT 5' ii) 3' CATGGCAA 5' iii) 5' CGCAATGG 3'

iv) 3' ACCGGACC 5' v) 5' ACGTTACC 5'
(9 pts) 4. (a) How can you account for the fact that tryptophan has a lower isoelectric point than histidine, even though both have amine nitrogen atoms in five-membered rings?

tryptophan is less basic than histidine because lone pair of tryptophan's N is part of π-system
⇒ tryptophan remains neutral (unprotonated) to lower pH ⇒ corresponds to lower isoelectric point

(b) Which nitrogen atom in the five-membered ring of histidine is more basic? (Circle the appropriate arrow.) Explain why this atom is more basic.

lone pair is not involved in π-system ⇒ available to act as a base

+3 pts for arrow
5. Consider the following molecular structures.

(a) Give the letter of the molecule(s) that can be classified as a wax.  

(b) Give the letter of the molecule(s) that can be classified as a steroid.  

(c) Give the letter of the molecule(s) that can be classified as a phospholipid.  

(d) Give the letter of the molecule(s) that can be classified as a monoterpenes.
(9 pts) 6. Draw the structural formula for the form of each amino acid that is most prevalent at the specified pH. *Show all lone electron pairs and all charges.* Refer to Table 17.1

(a) aspartic acid at pH = 8

\[
\begin{align*}
p_I &= 3.0 \\
H_2N-CH-CO_2\text{H} &\quad H_2N-CH-CO_2\text{H} \\
\text{CH}_2\text{-CO}_2\text{H} &\quad \text{CH}_2\text{-CO}_2\text{H}
\end{align*}
\]

+1pt for correct amino acid structure (regardless of state of charge)
+2pt for correct state of charge (if amino acid is wrong, receive full credit)
(if state of charge is correct for the given structure)

(b) valine at pH = 6

\[
\begin{align*}
p_I &= 6.0 \\
H_3N-CH-CO_2\text{H} &\quad H_3N-CH-CO_2\text{H} \\
\text{CH}(\text{CH}_3)_2 &\quad \text{CH}(\text{CH}_3)_2
\end{align*}
\]

(c) lysine at pH = 1

\[
\begin{align*}
p_I &= 9.7 \\
H_3N-CH-CO_2\text{H} &\quad H_3N-CH-CO_2\text{H} \\
\text{(CH}_2\text{)}_4 &\quad \text{(CH}_2\text{)}_4 \\
\text{NH}_3 &\quad \text{NH}_3
\end{align*}
\]
(21 pts) 7. Draw structures for either the major organic products or the reagents needed for the following reactions. (It is **not necessary** to write a balanced reaction with respect to reagents and inorganic products.)

(a) \[ \text{H}_3\text{O}^+ \rightarrow \text{product} \]

(b) \[ \text{cyclohexene} \]
1) \(\text{BH}_3\)
2) \(\text{H}_2\text{O}_2 / \text{OH}^-\)

(c) \[ \text{CH}_3\text{CH}_2\text{CHO} \]
1) \(\text{CH}_3\text{MgBr} \) or \(\text{CH}_3\text{Li}\)
2) \(\text{H}_2\text{O} / \text{OH}^-\)

(d) \[ \text{pyridinium chlorochromate} \]

(e) \[ \text{cyclopentanone} \]
1) \(\text{H}_2\text{C}=\text{O} / \text{OH}^-\)
2) \(\text{H}_2\text{O}\)

(f) \[ \text{cyclopentanone} \]
\[ \text{PhNH}_2 \]

(g) \[ \text{H}_2\text{N}-\text{COOH} \]
\[ \text{product} \]

+3 pts each

+2 pt for wrong regiochem

+2 pt for wrong regiochem

full credit, even if syn addition to give trans product is not shown

full credit, even if \(\text{H}_3\text{O}^+\) or \(\text{H}_2\text{O}\) not shown

full credit for either or both
A common method for preparing esters is treatment of an acid chloride with an alcohol. For example benzoyl chloride with methanol gives methyl benzoate. Write a mechanism for this nucleophilic acyl substitution reaction.
(4 pts) 9. Which of the following molecules is ATP - an important energy source in biology? Circle the letter of the correct answer.

A

B

C

D

(4 pts) 10. Draw the structure of the hydrogen-bonded base pair formed between guanine and cytosine.
(10 pts) 11. Consider the Friedel-Crafts acylation of nitrobenzene.

\[
\text{NO}_2 \quad \xrightarrow{\text{H}_3\text{C}-\text{C}-\text{Cl}} \quad \text{NO}_2
\]

(a) Draw the structure for each of the three carbocation intermediates formed upon ortho, meta, and para attack on nitrobenzene.

\[\text{ortho} \quad \text{meta} \quad \text{para}\]

\[\text{etc} \quad \text{etc} \quad \text{etc}\]

Note: for ortho and para, it is not essential that they draw the particular resonance structure showing the charge near -NO_2 group.

(b) Use the structures in part (a) to explain the observed selectivity for meta substitution.

ortho and para attack both place (+) charge next to the strongly electron-withdrawing -NO_2 group. Therefore, ortho-attack is strongly disfavored.

meta attack avoids this problem \(\Rightarrow\) is observed

+4 pts good answer
+2 pts OK answer
+0 pts wrong or blank
12. For each of the following cyclohexane derivatives, draw two different chair conformations and indicate which one is more stable.

(a) For (a) it students good-up the structure (i.e., cis/trans, 1,2- or 1,4-substitution). Deduct 2 pts for one structure, but give 2 pts if the 2nd structure is the correct ring inversion structure and give 2 pts if their analysis of stability is consistent with the structures.

(b) For (b), bulky tert-butyl group has stronger preference to remain axial, not necessary to give explanation.
(6 pts) 13. Arrange the following compounds in order of increasing reactivity toward electrophilic aromatic substitution.

\[
\text{d} < \text{b} < \text{c} < \text{a}
\]

*least reactive*  
+2 pts for this regardless of others

*most reactive*  
+2 pts for this regardless of others

(12 pts) 14. Draw Newman projections for the staggered and eclipsed conformations of propane, CH\textsubscript{3}CH\textsubscript{2}CH\textsubscript{3}, specify which conformation is more stable, and BRIEFLY explain why it is more stable.

**Staggered** +2 pts

**Eclipsed** +2 pts

Staggered is more stable because it experiences less steric congestion. Eclipsed contains steric repulsion / violation of van der Waals radii between CH\textsubscript{3} + H.
(12 pts) 15. Consider the following \( S_N^2 \) reaction:

\[
\begin{align*}
&\text{primary} \\
&\text{+2 pts each} \\
&\text{Br} &\text{OH} &\text{OH} &\text{Br} \\
&\text{SN2}
\end{align*}
\]

Circle the correct response to each of the following questions:

T  F  (a) Both the alkyl halide and the nucleophile are involved in the transition state for the rate determining step.

T  F  (b) Mechanistically speaking, the reaction proceeds with retention of configuration.

T  F  (c) The reaction proceeds with loss of optical activity.

T  F  (d) The order of reactivity is tertiary (fastest) > secondary > primary > methyl (slowest).

T  F  (e) The greater the steric crowding around the reactive center, the lower the rate of reaction.

T  F  (f) The rate of reaction is greater with good nucleophiles compared with poor nucleophiles.