Chemistry 210

Final Examination

2.0 h; 240 points

Dr. Kathleen Nolta

First Name ________________________

Last Name ________________________

Signature ________________________

UM ID # ________________________

Problem | Points | Score | GSI
---|---|---|---
I | 42 | | |
II | 35 | | |
III | 36 | | |
IV | 46 | | |
V | 42 | | |
VI | 39 | | |
Total | 240 | | |

Precision in drawing counts. Check all three-dimensional representations to ensure you are implying an unequivocal direction of bonding. Do not forget to include important features such as nonbonding electron pairs and formal charges when appropriate. Individual point values are given in the corner of each answer space. The exam has 6 pages in addition to this cover page. A pKa table is on the last page.
I. (42 points)

A. The compound shown below is a commonly prescribed antifungal drug. It belongs to a category of compounds known as triazoles. Analyze the geometry and other properties for various atoms in this drug.

![Diagram of the compound]

(a) Find all tetrahedral chiral centers in this compound and give them appropriate stereolabels

(b) For all the rings indicated, count the number of electrons held in p orbitals for all ring atoms.

(c) How many aromatic rings are in this molecule?

(d) Put a box around the shortest C-O bond in this molecule.

B. For each of the atoms indicated with an arrow, provide the atom’s most reasonable hybridization as well as its electronic geometry (VSEPR) and observable geometry (write none if it is not observable).

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<th>hybridization</th>
<th>electronic geometry</th>
<th>observable geometry</th>
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</table>

C. The triazole ring is shown below. Draw a complete set of all closed shell resonance contributors for this molecule; atomic formal charges should be +1, 0, or -1. Then circle the best of the ones you have drawn.

![Diagram of the triazole ring]

Provide an accurate and complete three-dimensional orbital picture for this triazole ring (considering all valid resonance contributors when you assess hybridization for each atom). You should use lines, dashes, wedges, and p orbitals (lone or overlapping) to show the direction of all electrons (or empty orbitals) in your drawing. Show all bonds and all bond angles should reflect the appropriate geometry and hybridization chosen for your drawing.
II. (35 points)  

A. A sulfur-chlorine bond reacts in addition reactions like mixed halogens; the sulfur atom is the electrophilic site and it forms a halonium-like cyclic intermediate. Show the curved arrow mechanism for the formation of this intermediate. Though stereoisomers form, you should draw only one intermediate and the final product formed from this intermediate, showing stereochemistry clearly.

B. Predict the main organic products (not byproducts) of these multi-step transformations; if stereoisomers form, draw one and write "+ enantiomer" or "+ diastereomer" in the box.

C. This transformation combines complexation, electrophilic aromatic substitution and rearrangement! It starts with a complexation reaction, which generates a leaving group and an electrophilic C. The pi bond in the smaller ring nucleophilically attacks the electrophilic carbon, forming a new 5-atom ring and a carbocation resonance-stabilized by the adjacent nitrogen. A ring expansion generates a new carbocation and in step 4, a final proton transfer returns the ring's aromaticity (you may use a generic :B).
III. (36 points)

A. Each of the following transformations demonstrates some form of selectivity. Provide the other information requested.

(a) (i) Draw the starting material

(ii) Draw a Newman projection for the most stable conformation of the bond highlighted in the product. Use the view indicated and consider steric only.

(b) Selectivity in proton transfers occurs by choosing your reagent wisely. The most acidic proton in compound A has a pKa ~3.5, while the second has a pKa ~10. If treated with an excess of the following bases, which will result in a "zwitterionic" (two oppositely charged atoms) form of compound A (removing most of the first proton, while leaving the second relatively untouched).

(c) (i) Draw the product

(ii) Draw the product

B. For each of the following connectivity drawings check all the descriptions that apply.
IV. (46 points)

In each of the following reactions more than one product is formed. Draw each product; be sure to show all structural and stereochemical properties unambiguously. When regioselection is predicted, draw only major regioisomers. Note that sometimes you are given extra guidance about where to put your product(s). Also, provide the NMR information requested and analyze your products, depending on the problem.

A. \[ \text{CH}_3 \text{CH} = \text{CH}_2 \text{HNO}_3 \xrightarrow{\text{H}_2\text{SO}_4 \text{ (cat.)}} \]

Draw all products

These products are (check all that apply):

- enantiomers
- diastereomers
- structural isomers

Which of these products is/are optically active? (check one)

- One
- Both
- Neither

B. \[ \text{CH}_3 \text{CH} = \text{CH}_2 \xrightarrow{\text{H}_2 \xrightarrow{\text{Pd/C}} \text{H}_2\text{O}} \]

Draw all products

The NMR spectra for B would show:

(write in the number)

- $^{13}$C NMR signals
- $^1$H NMR signals

Which of these products is/are optically active? (check one)

- One
- Both
- Neither

C. \[ \text{CH}_3 \text{CH} = \text{CH}_2 \xrightarrow{1) \text{BH}_3} \xrightarrow{2) \text{H}_2\text{O}_2} \]

Draw all products

These products are (check all that apply):

- enantiomers
- diastereomers
- structural isomers

Which of these products is/are optically active? (check one)

- One
- Both
- Neither

D. \[ \text{CH}_3 \text{CH} = \text{CH}_2 \xrightarrow{\text{H}_2\text{SO}_4 \text{ (cat.)}} \]

Draw major product(s)

The NMR spectra for D would show:

(write in the number)

- $^{13}$C NMR signals
- $^1$H NMR signals

E. \[ \text{CH}_3 \text{CH} = \text{CH}_2 \xrightarrow{\text{H}_2\text{SO}_4 \text{ (cat.)}} \]

Draw all products

These products are (check all that apply):

- enantiomers
- diastereomers
- structural isomers

Which of these products is/are optically active? (check one)

- One
- Both
- Neither
V. (42 points)

A. The chemical transformation shown below consists of some very familiar Chemistry 210 reactions. Provide the missing details for this multi-step process. Be sure to read the specific prompts carefully - sometimes curved arrow mechanisms are requested, and sometimes transition state drawings or intermediates are requested.

(a) Provide the curved arrow mechanism - step 1

(b) Provide the curved arrow mechanism - step 2

(c) Provide a drawing of the transition state

(d) Provide the curved arrow mechanism - step 3

(e) Provide a drawing of the transition state

(f) Draw the intermediate and the curved arrow mechanism for the last step

(g) Assign stereolabels to all chiral centers in the product, P

B. Consider the energy diagram below, which might be used to illustrate the reaction above.

(a) Using positional labels, state how you would calculate the following (give your answer as a mathematical equation, like "X minus Y")

(i) the $E_a (\Delta G_{ts})$ of the rate determining step for the reverse transformation?

(ii) the $\Delta G$ for the second step in the reverse transformation?

(iii) the $E_a (\Delta G_{ts})$ of the second step for the formation of P from SM?

(b) In this diagram, what positional label(s) represent(s) the drawing you provided in box c of part A above?

(c) In this diagram, using positional labels, what represents the drawing you provided in box f of part A above?
VI. (39 points)

A. For each of the following molecules, choose all the descriptions that apply; write the letters corresponding to those descriptions in the box with the drawing you are analyzing.

(a) [Drawing of molecule a]
   - A) has an enantiomer
   - B) has an achiral diastereomer
   - C) has a chiral diastereomer
   - D) is optically active
   - E) is meso

(b) [Drawing of molecule b]
   - F) contains an R stereocenter

B. (a) If you remember your second midterm, you might recall that you were asked to evaluate chair conformations for molecules like (and including) this one. Draw all the biomolecular elimination products that would result from this starting material. Then consider the effects of the changes suggested.

   [Diagram of reaction with SM, CH₃CH₂O, Na, and Br]

   (b) Draw the chair conformation that is preferred for the E2 reaction shown above. As always, be sure to clearly and accurately show the axial and equatorial positions for all substituted ring atoms. You do not have to show axial and equatorial hydrogen atoms for unsubstituted ring atoms.

   [Diagram of chair conformation]

   (c) For each of the following pairs, choose all the descriptions that apply; write the letters corresponding to those descriptions in the box with the drawings you are analyzing.

   (i) [Drawing of molecules a and b]
      - a and b are:

   (ii) [Drawing of molecules c and d]
      - c and d are:

   (iii) [Drawing of molecules e and f]
      - e and f are:
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