**Chemistry 210**

**Second Examination**

1.5 h; 120 points

Dr. Kathleen Nolta

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**PRINT THE FIRST LETTER OF YOUR LAST NAME HERE:**

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<table>
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<th>Problem</th>
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<td><strong>Total</strong></td>
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_Complete Lewis structures are required unless you are given other specific instructions. 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. (22 points)

A. For each of the compounds shown below:
   (1) Identify any sources of stereochemistry by circling the site(s) and providing appropriate stereolabel(s) for each site. If no stereochemistry is present, write "none."
   (2) Then choose the statements that can be used to describe that molecule.
   (3) Provide information about the expected NMR spectra for those compounds specified.

   Identify and label any source(s) of stereochemistry
   "Check" all descriptions that apply

   ![Chemical Structure 1](image1)
   "Check" all descriptions that apply
   - has a meso compound
   - has at least one chiral diastereomer
   - has an enantiomer
   - has at least one achiral diastereomer
   - has a meso stereoisomer
   The NMR spectra for 1 would show:
   (write in the number)
   - $^1H$ NMR signals

   Identify and label any source(s) of stereochemistry
   "Check" all descriptions that apply

   ![Chemical Structure 2](image2)
   "Check" all descriptions that apply
   - is a meso compound
   - has at least one chiral diastereomer
   - has an enantiomer
   - has at least one achiral diastereomer
   - has a meso stereoisomer
   The NMR spectra for 2 would show:
   (write in the number)
   - $^{13}C$ NMR signals

   Identify and label any source(s) of stereochemistry
   "Check" all descriptions that apply

   ![Chemical Structure 3](image3)
   "Check" all descriptions that apply
   - is a meso compound
   - has at least one chiral diastereomer
   - has an enantiomer
   - has at least one achiral diastereomer
   - has a meso stereoisomer

B. For each of the pairs shown below, choose the statements that can be used to describe the drawings and their relationship, if a relationship exists.

(a) ![Chemical Structure 4 and 5](image4)

   "Check" any/all descriptions that apply
   - are enantiomers
   - are diastereomers
   - are structural isomers
   - are conformational isomers (conformers)
   - are identical molecules
   - contain at least one R stereocenter (in the pair)
   - represent at least one achiral compound

(b) ![Chemical Structure 6 and 7](image5)

   "Check" any/all descriptions that apply
   - are enantiomers
   - are diastereomers
   - are structural isomers
   - are conformational isomers (conformers)
   - are identical molecules
   - contain at least one R stereocenter (in the pair)
   - represent at least one achiral compound

II. (26 points)

A. As an extension of the electrophilic additions you learned about in class, it turns out that pi bonds can often react with other pi bonded atoms in "cycloaddition" reactions, leading to the formation of ringed structures, like molecule 1 shown below. Consider the one-step reaction shown below and provide the missing information.

(i) provide the curved arrow mechanism for this reaction

(ii) draw the transition state for this one-step reaction.

(iii) In fact, the ketene shown above can react in the same sort of cycloaddition reaction with another ketene, and structurally isomeric products form. Draw the two possible cycloaddition products that result, using the NMR data provided.

B. The following substitution reaction yields two products (rather than the one expected in bimolecular substitution). In the first step, the leaving group leaves with the formation of a resonance stabilized carbocation. In the second step, the nucleophilic attack leads to the formation of the products shown. Provide the requested information.

(a) draw the curved arrow mechanism for the first step

(b) draw the product(s) from the first step (all closed shell)

(c) draw the transition state for the second step, leading to the products shown

(d) Complete a sketch of the energy diagram for this reaction; you should label the positions of molecules/events occurring in boxes (b) and (c), as well as showing the position of the products. Relative energy levels should reflect the kinetic and thermodynamic information given in the scheme at left.
III. (28 points)

A. Prednisone is a synthetic steroid that is commonly prescribed for allergic reactions. Unfortunately, it also happens to be a phenomenal immunosuppressant.

(i) Identify all chiral stereocenters in prednisone. Label each with an R or an S.

B. Molecule 1 is a minor product of the reaction shown. Answer the other questions about this reaction and its products.

(ii) How many total products are expected to form in this reaction; include major and minor products in your calculation.

   - optically active product(s)  
   - optically inactive product(s)

(iii) Draw the two chair conformations for 1 and indicate the $K_{eq}$ for your pair of chairs. 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.

(iii)
A. Carnitine is an important biomolecule that plays an essential role in the trafficking of fatty acids to the mitochondria for oxidation and the production of cellular fuel. Analyze the conformational chemistry of the two main C-C bonds in carnitine by drawing Newman projections as directed.

(i) Draw a Newman projection of the C₃-C₂ bond in the conformation shown; view with the C₃ in front.

(ii) Draw a Newman projection of the C₁-C₂ bond in the conformation shown; view with the C₁ in front.

(iii) The ionic attraction within this molecule leads to a favorable gauche interaction. Show this staggered conformation using a Newman viewing down the C₂-C₃ bond.

B. Each of the drawings below shows only the connectivity of a molecule or a set of molecules that share this connectivity. For each, check all the statements that can be used to accurately describe this connectivity and the molecule(s) represented by this connectivity.

(i) This connectivity represents:

- only 1 unique compound; no stereoisomers exist
- only 2 enantiomeric compounds
- only 2 diastereomeric compounds
- exactly 3 different molecules
- 4 or more different molecules
- only optically inactive molecules
- only optically active molecules

"Check" any/all descriptions that apply to this connectivity

(ii) This connectivity represents:

- only 1 unique compound; no stereoisomers exist
- only 2 enantiomeric compounds
- only 2 diastereomeric compounds
- exactly 3 different molecules
- 4 or more different molecules
- only optically inactive molecules
- only optically active molecules

"Check" any/all descriptions that apply to this connectivity
V. (25 points)

A. Naming fun! Convert name to structure or structure to name as needed. Be sure to include all information on connectivity and stereochemistry in both your drawings and your naming. And then fill in the missing information about the NMR spectrum for each compound.

(i) Draw this compound:  
(S)-1,3,4,4-tetramethylcyclopent-2-en-1-ol

(ii) Name this compound:

Spectra taken on this compound should show:  
☐ $^{13}$C NMR signals  
☐ $^1$H NMR signals with ratio

B. The following reactions yield only two different products that share the same molecular formula. These products form in approximately the same concentration, too. Draw the two different products, showing all information necessary to define the molecule, and describe their relationship by checking the appropriate box.

(i)  
\[ \text{H}_3\text{C} \quad \text{C} = \text{C} \quad \text{CH}_3 \]  
\[ \text{HBr} \quad \text{1 equivalent} \]  
\[ \quad \quad \quad \text{Draw the two different products} \]  
\[ \quad \quad \quad \text{The relationship between these two products is:} \]  
☐ enantiomers  
☐ diastereomers  
☐ structural isomers

(ii)  
\[ \text{C}_9\text{H}_{17}\text{Cl} \]  
\[ \text{HCl} \quad \text{1 equivalent} \]  
\[ \quad \quad \quad \text{Draw the two different products} \]  
\[ \quad \quad \quad \text{The relationship between these two products is:} \]  
☐ enantiomers  
☐ diastereomers  
☐ structural isomers

(iii)  
\[ \text{Draw the two different products} \]  
\[ \text{The relationship between these two products is:} \]  
☐ enantiomers  
☐ diastereomers  
☐ structural isomers
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