Name: _____

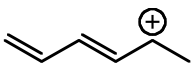
Chem 12A
September 25, 2009

Exam 1
show all work!!

Exam 1 is worth 10% of your grade (50 points). You are allowed to use one 3"x5" index card for notes, a pKa table, the trends, tools, etc. handout, and a Periodic Table. Show all work for full credit. Write your answers legibly. You may ask me for a hint; however, each hint will cost you 1 point.

1. (4 points) Agree or disagree with the following statements. Support your answer with chemical reasoning, calculations, analogies, examples, etc.

a. Structure 1 and Structure 2 are isomers of each other. (Next time: Structures 1 and 2 are resonance structures. Over how many atoms are the + charge and pi electrons shared?)



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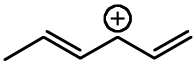

2

b. See Structure 1 in Question 1a. The carbon with the positive charge is sp^2 hybridized with a trigonal planar geometry.

2. (4 points) a. Is Structure 2 from Question 1 a cis or trans, or E or Z alkene? If so, identify the double bond and name the isomer.

b. Structure 2 can act like a nucleophile or electrophile. Is this structure a better nucleophile or better electrophile? Give reasons.

3. (16 points) Isopropanol (2-propanol, rubbing alcohol) is a common solvent that is mainly used to dissolve components of shellac and other resinous finishes. It can be oxidized to make acetone, CH_3COCH_3, another common organic solvent.

a. Three possible resonance structures for acetone are shown below. Use curved arrow to show how the first and third resonance structures are derived from the second. Is each resonance structure equivalent? If not, which resonance structure is the minor (least important) contributor? Give reasons.

(show ChemDraw)

b. Compare structure 1 to structure 2. Briefly describe how IR spectroscopy can be used to distinguish these two structures.

c. Acetone has a pK_a of 19 whereas acetic acid has a pK_a of 4.7. Which substance requires a stronger base to remove its proton? Give reasons.

d. The conjugate base of acetone has two possible resonance structures. Draw each resonance structure. Which structure is the major contributor? Give reasons.

4. (26 points) The diagram below shows reactions involving isopropanol and other organic compounds.

a. For Reactions 1, 2, 3, and 4, determine the reaction conditions.

b. Compare Reactions 1 and 2. Which method gives a higher yield of 2-chloropropane? Give reasons.

c. Substitute ethanol (C_2H_5OH) for isopropanol in Reaction 1. Which alcohol reacts faster with HCl? Give reasons.

d. For Reaction 1, write the mechanism. For each step, use curved arrows to show bonds breaking and forming, identify the nucleophile and electrophile (for a polar reaction), and elemental mechanistic process. Draw a reaction energy diagram. Identify the rate determining step.

Name: _____

Chem 12A
November 6, 2009

Exam 2
show all work!!

Exam 2 is worth 10% of your grade (50 points). You are allowed to use one 3"x5" index card for notes, a pKa table, the trends, tools, etc. handout, and a Periodic Table. Show all work for full credit. Write your answers legibly. You may ask me for a hint; however, each hint will cost you 1 point.

1. (4 points) Agree or disagree with the following statements. Support your answer with chemical reasoning, calculations, analogies, examples, etc.

a. Achiral reactants can produce chiral products.

b. When a 1-bromobutane reacts with $NaOC_2H_5$, the elimination product is the major product. For full credit, draw the structure of the major product.

2. (6 points) a. Idenitify the following pair of compounds as either enantiomers, diastereomers, constitutional isomers, the same compound, or different compounds. If the compounds are enantiomers, determine the configuration (R or S) at each chirality center.
(cis and trans -1, 2-dibromocyclopentane)
b. One of the compounds from part a can be synthesized by treating an alkene with bromine. Identify the compound and give reasons for your choice.

3. (5 points) Starting with an alkane with 5 carbons or less, describe a synthesis of acetone, $(CH_3)_2CO$.

4. (8 points) The following compounds are responsible for hot and spicy sensations or cool and minty sensations. Which of these compounds is/are chiral? For the chiral compounds, circle the chirality centers.
(limonene, capsaicin, carvone, menthol)

5. (7 points) a. You want to replace the OH group in menthol (see structure in Question 4) with OCH_3 or with Cl. If you want to minimize the formation of the elimination product, which substitution is easier to accomplish? Give reasons.
b. Describe a synthesis method to accomplish this substitution reaction.

6. (20 points) Let's say you've eaten some mint that contains menthol (see structure in Question 4) which gives food a cool and minty taste.
a. If menthol has a chirality center(s), determine the number of stereoisomers and the configuration (R or S) at each center.
b. Menthol reacts with an equimolar amount of HCl in your stomach to form a mixture of products. Draw the structure of the major product. Briefly explain why this product is the major product. Is this product optically active? Give reasons.
c. For your reaction in part b, write the reaction mechanism. For each step, use curved arrows to show bonds breaking and forming, identify the nucleophile and electrophile (for a polar reaction), and elemental mechanistic process.

Chem 12A Fall 2009 Lab Notebook and Lab Safety Factor
Due Wednesday, December 9, 2009

Your Lab Notebook and Lab Safety Factor Grade is worth 5% of your overall course grade.
1. For your lab notebook, give yourself a grade (A – F) based on the following criteria. Be honest and be fair to yourself. Don't be too easy but don't be too harsh either. Then, give yourself an overall lab notebook grade.

Criteria	Grade
Labs 1 through 14 entered in sequential order	
Each lab shows a flow chart, relevant chemical equations, properties, and calculations, table of data and results, discussion, and conclusions	
Appropriate details so another organic chemistry student can follow what you did in each experiment	
Overall Lab Notebook Grade	

2. For your lab safety factor grade, give yourself a grade (A – F) based on the following criteria. Be honest and be fair to yourself. Don't be too easy but don't be too harsh either. Then, give yourself an overall lab safety factor grade.

Criteria	Grade
Attendance (including <u>being on time</u>)	
Your timely submission of lab assignments	
Your observation of lab safety rules and regulations	
Your lab technique	
Your initiative and cooperation	

Overall Lab Safety Factor Grade	

3. **Combined** Lab Notebook and Lab Safety Factor Grade: _____

4. a. Do you believe the lab portion of this course helped you learn organic chemical reaction principles?
b. Ignoring poor product yields and not having an IR, which lab do you think was the most helpful in learning organic chemistry? Give reasons.
c. Which lab do you think was least helpful in learning organic chemistry? Give reasons.

Did you have enough or adequate help in this course (lecture or lab or both)? What could have made it better?

Chem 12A, FINAL EXAM - TAKE-HOME PART
due Wednesday, December 18, 2009 at 11:30 am

The Take Home Part of the Final Exam is worth 10% of your grade (50 points). For full credit, show all work in a logical and legible sequence. Clearly underline or circle your final answer. Include units where needed. You may work in groups on Questions 1 – 3 of the Final Exam. **You must do Question 4 on your own.** If you work in a group, make sure every member contributes to the solutions. Turn in one set of solutions with the names of each member of your group. If you discuss any question or part of a question with another student, you are working in a group.
1. (15 points) a. (i) Name two organic compounds that are useful in real life. Your organic compound must have at least three carbon atoms. Give the chemical name, chemical formula, and briefly describe this compound's usefulness.
(ii) Draw the Lewis structure of each compound. Circle the functional group(s) in each compound. Next to each circle, give the name of the functional group.
(iii) Put a square around one of the carbons. Determine the valence bond hybridization at this carbon. Then, identify the molecular geometry at this atom.
b. Sketch an IR spectrum of each compound. For each band, identify the bond vibration, e.g., C-H stretch.
c. Describe how you would synthesize each compound starting from acetylene or benzene.
d. Show the mechanism of each reaction. For each step in your mechanism, identify the nucleophile and electrophile (if a polar mechanism), push electrons to show bonds breaking and forming, and identify the elemental mechanistic process.
e. Draw a reaction energy diagram for each reaction.

2. (15 points) Chemical and Engineering News occasionally publishes a column called "What's That Stuff?" Go to the "What's That Stuff" website (http://pubs.acs.org/cen/whatstuff/stuff.html). Click on Dental Anesthetics. Read the article. Use and apply your knowledge of chemistry and science to describe how Dental Anesthetics works.
a. According to this article, how do anesthetics work?
b. A common topical anesthetic, which is a disubstiituted benzene, is mentioned in this article. Give the name and draw the structure of this compound. Starting from a monosubstituted benzene, describe how you would synthesize this compound. (Start or stop your synthesis from or at the acid.)
c. The structure of Lidocaine is shown in the article. Starting from benzene, describe a synthesis of lidocaine. For the amine substituent, use the NH_2 group rather than the amide.
d. The structure of Articaine is shown. Is articaine optically active? If so, identify the chirality center(s). Is articaine aromatic? Give reasons.
e. Consider the electrophilic aromatic substitution reaction of 3-methyl thiophene with E-Y, where E is an electrophile. Show the mechanism of this reaction. Use curved arrows to show bonds breaking and forming. Identify the elemental mechanistic process for each step. Explain the position in the thiophene ring where a second substituent would substitute.

The S has two lone pairs. Are the two lone pairs equivalent? If not, which lone pair is the stronger nucleophile?

3. (10 points) Consider the bromination reactions of cis-2-butene and trans-2-butene. In each reaction, the product is 2, 3-dibromobutane:

cis-2-butene + Br_2 ----> 2, 3-dibromobutane (1)

trans-2-butene + Br_2 ----> 2, 3-dibromobutane (2).

a. Note that 2, 3-dibromobutane has two chiral carbons. Using Fisher projections, draw the stereoisomers of 2, 3-dibromobutane. Determine the configuration at each chiral carbon. Determine which stereoisomers are enantiomers, diastereomers, or meso compounds.

b. In one reaction, enantiomers are formed. In the other reaction, a meso compound is formed. Show the mechanism of each reaction. In each mechanism, show the stereochemistry of each intermediate by using dashes and wedges. For the products that are formed, determine the configuration at each chiral carbon.

4. (10 points) According to the Chem 12A Course Information Handout, your "grade will be based on your performance and mastery of the last Course Objective." Each course objective is shown below.
a. For each objective, give yourself a grade (A – F) that reflects your understanding of that objective. Be honest and be fair to yourself. Don't be too easy but don't be too harsh either
b. Identify the course objective that you understand the best. What did you do to help you understand this objective so well?
c. Identify the course objective that you understand the worst. What could you have done to understand this objective better?
d. The following terms were used in Chem 12A: inductive effect, steric effect, resonance stabilization, carbocation intermediate, regioselective, stereoselective, stereospecific, activating/deactivating group. Match the term to the appropriate course objective. Give one example of how this term is associated with this objective.
e. Give yourself an overall course grade based on your understanding of the course objectives. (The grade you give yourself may not be your official course grade. Your instructor will determine your overall course grade.)

Objective	Description	Grade
1	classify and name organic compounds by functional group	
2	relate the structure, bonding, and geometry of organic compounds to properties, such as reactivity	
3	identify common nucleophiles and electrophiles	
4	identify common organic mechanistic processes and show electron flow in organic reaction mechanisms (*curved arrows*)	
5	understand reactivity principles and trends	
6	apply and relate (3), (4), and (5) to predict conditions and products of organic reactions, e.g., substitution and elimination reactions of alkyl halides	
7	design syntheses of organic compounds	
8	relate structure and reactivity to stereochemistry	
9	perform organic laboratory techniques to separate, isolate, and identify organic compounds	
10	identify and distinguish between different characterization methods, e.g., IR and NMR, for organic compounds	
	Overall Chem 12A Grade	

Name: _____

Chem 12A
December 18, 2009

FINAL EXAM
Show all work!!

The Final Exam is worth 10% of your grade (50 points). You are allowed to use one 8.5"x11" page for notes, a pK_a table, the trends, tools, etc. handout. Show all work for full credit. Write your answers legibly. You may ask me for a hint; however, each hint will cost you 1 point.
1. (6 points) Agree or disagree with the following statements. Support your answer with chemical reasoning, calculations, analogies, examples, etc.
a. Toluene undergoes bromination faster than chlorobenzene which is faster than phenol.
b. The reaction mechanism of the polymerization of polypropylene and polystyrene are similar in that a primary radical is formed in the propagation step: RO• + propylene or styrene → 1^o radical. For full credit, draw the structure of the radical.

c. To control whether a substitution or elimination reaction occurs in an alkyl halide or alcohol, the leaving group is the only important factor.

2. (10 points) In 2001, chemistry professor Hideo Tomioka, graduate student Eri Iwamoto, and coworkers at Mie University, Tsu, reported the generation of triplet bis(9-anthryl)carbene by photolysis of a precursor diazomethane [*Nature,* **412**, 626 (2001)]. The half-life of this carbene (shown below) is 19 minutes in solution at room temperature which is more than twice as long as the previous most stable carbene which had a half-life of nine minutes. (Note: a carbene is a neutral molecule in which one of the carbons has 6 valence electrons, is bonded to two other atoms with no multiple bonds.)
a. Draw a resonance structure of this carbene. Use curved arrows. Are these resonance structures equivalent? If not, which resonance structure is more stable? Give reasons. Why do you think this carbene is so stable?
b. This compound contains 8 rings. Which ring(s) is/are aromatic? Give reasons.
c. Is the entire compound aromatic? Give reasons.

3. (9 points) Acetylene, ethylene, and benzene are common starting materials in organic synthesis.
a. Using acetylene, ethylene, or benzene, give an example of a reaction that is used to increase the carbon chain length. Include the structure of the reactants, reaction conditions and structure of the product.
b. Using acetylene, ethylene, or benzene, give an example of a reaction that is used to decrease the carbon chain length. Include the structure of the reactants, reaction conditions and structure of the product.
c. Using acetylene, ethylene, or benzene, give an example of a reaction that is used to convert a carbon chain into a carbon ring. Include the structure of the reactants, reaction conditions and structure of the product.

4. (12 points) You need some acetone, $(CH_3)_2CO$, to remove paint but all the stores are closed. You have some acetylene and some isobutane (2-methylpropane) and figure you can use your knowledge of organic chemistry to make acetone.
a. Starting from isobutane, describe how to synthesize acetone. Include the reaction conditions in each step of your synthesis.
b. Starting from acetylene, describe how to synthesize acetone. Include the reaction conditions in each step of your synthesis.
c. Compare your synthesis methods. Which method gives a higher yield of acetone? Give reasons.

5. (13 points) Compare limonene (see Compound A, one of the compounds that is responsible for the tangy odor in lemons) to Compound B and Compound C.
a. Predict the product(s) of Reactions 1-6.
b. For one of these reactions, you can control the product distribution by lowering the temperature from room temperature to $-80^{o}C$. In which reaction is the product distribution controlled by temperature? What is the product distribution at each temperature? Give reasons.
c. For Reaction 6, explain why your product is produced.