Chem 12A Fall 2014

Quiz 1, September 10, 2014

1. Draw the bond-line (skeletal) structure of CH₃CHOHCHCBrCH₃.

b. Circle the atom(s) that have sp^2 hybrid orbitals.

c. The O in this compound is basic. Use curved arrows to show the reaction between this compound and HCI. Draw the structures of the products.

2. a. What is the chemical formula of the compound shown below?

b. Use curved arrows to transform the resonance structure shown to another resonance structure.



c. Are the resonance structures equivalent? If not, which structure is the major contributor? Give reasons.

Name: _____

Chem 12A October 6, 2014

(ii) weakest base that reacts with ROH

EXAM 1

show all work!!

Exam 1 is worth 10% of your grade. You are allowed to use <u>one</u> 3"x5" index card for notes. Show all work for full credit. Write your answers legibly. You may ask me for a hint; however, each hint will cost you 0.25 units.

Table 1. Acidity Constants (pK_a) of Acids.

Acid		HCI	R_2OH^+	ROH_2^+	H ₃ O ⁺	RCOOH	H ₂ O	ROH	RCOCH ₃	NH_3	RH
pK _a	-10	-4	-3	-2	-1.7	5	15.7	16	19	35	50
Base	RCHO		ROR								

1. (1 unit) Table 1 shows the pK_a's of various acids. Draw the Lewis structure of the:

(i) conjugate acid of RCHO (aldehyde) and a resonance structure

2. (2.5 units) Aspartame, a sugar substitute, has two chirality centers. The S,S isomer fits into the sweetness receptor site whereas the S,R isomer does not. (The configuration order is from left to right on the structure below.)



aspartame

- a. Place a * on each chirality center.
- b. How many stereoisomers of aspartame exists?
- c. In the structure above, draw a C-H bond to each chirality center using a wedge or dash to show the S,S isomer.
- d. Is the S,R isomer (bitter) isomer an enantiomer, diastereomer, or meso compound of the S,S (sweet) isomer?

e. Which H is the most acidic proton? Circle this proton.

3. (1.5 units) Six sided rings are found in biomolecules. Two conformers of glucopyranose are shown below.





β-D-glucopyranose

a-D-glucopyranose

a. Circle the more stable glucopyranose conformer.

b. In general, 1,3 diaxial interactions cause strain in a ring. Box the atoms or groups that cause the most strain in the less stable conformer of glucopyranose.

c. The lone pair on O is basic. Triangle the O that is the weakest base in β -D-glucopyranose.

d. Does Structure C represent β -D-glucopyranose or α -D-glucopyranose?



Structure C

4. (1.5 units) a. Four compounds (A-D) are shown below. Identify the specified pair as constitutional isomers, stereoisomers, or the same compound. If they are stereoisomers, are they enantiomers or diastereomers?



(ii) Is this compound chiral?

b. Using Table 1, draw the structure of the weakest base (Base 1) that reacts with Compound 1 to form the Intermediate. Use curved arrows to show how Base 1 reacts with Compound 1 to form the Intermediate. Draw the structure of the Intermediate and resonance structures as needed. If there are resonance structures, identify the major contributor. c. Using Table 1, draw the structure of the weakest acid (Acid 1) that reacts with the Intermediate to form Compound 2. Use curved arrows to show how Acid 1 reacts with the Intermediate to form Compound 2. d. Using Table 1, draw the structure of the weakest base (Base 2) that reacts with Compound 2 to form the Intermediate. Use curved arrows to show how Base 2 reacts with Compound 2 to form the Intermediate. e. Using Table 1, draw the structure of the weakest acid (Acid 2) that reacts with the Intermediate to form Compound 1. Use curved arrows to show how Acid 2 reacts with the Intermediate to form Compound 1.

f. Is Compound 1 a stronger or weaker acid than Compound 2? Stronger Weaker

g. Look at the structure of the Intermediate that you drew in Question 5b. Once this Intermediate forms, is Compound 1 or Compound 2 more likely to form? Give reasons.

Quiz 2, October 22, 2014 pK_a 's: HBr = -9, ROH₂⁺ = -2, H₃O⁺ = -1.7, H₂O = 15.7 1. Use curved arrows to show how: (draw in H's as needed)

- a. Compound 1 is converted to Compound 2,
- b. Compound 2 is converted to Compound 3,
- c. Compound 2 reacts with H₂O to form Compound 4. Draw the structure of Compound 4.
- 2. Identify Reagents A, B, C, and D.
- 3. Compound 1 is converted to Compound 5. Is the mechanism S_N1 or S_N2?



Name: _____

Chem 12A November 12, 2014

EXAM 2 show all work!!

Exam 2 is worth 10% of your grade. You are allowed to use one 3"x5" index card for notes. Show all work for full credit. Write your answers legibly. You may ask me for a hint; however, each hint will cost you 0.25 units. Table 1 Acidity Constants (nK_a) of Acids

Acid	H ₂ SO ₄	HI	HBr	HCI	R ₂OH ⁺	ROH_2^+	H ₃ O ⁺	RCOOH	H ₂ O	ROH	NH ₃
pKa	-9	-9	-8	-4	-3	-2	-1.7	5	15.7	16	35

1. (2.5 units) Structural features gives us clues as to how a compound reacts.

a. In the compound below, circle the alpha carbon(s), draw in the H's bonded to the beta carbon(s), box the nucleophilic atom(s). Does this compound contain a leaving group(s)? If you identify more than one leaving group, which one is the better leaving group?



b. The compound in part a reacts with $NaOC_2H_5$. Draw the structure of the intermediate that forms. If excess $NaOC_2H_5$ is present, what happens next?

c. The compound in part a reacts with sulfuric acid. Draw the structure of the intermediate that forms. Then, the intermediate reacts with water. Draw the structures of the substitution product and elimination product that forms.

2. (1 units) Carbocations are intermediates in reactions that we have looked at in Chem 12A. Show the <u>three</u> things that can happen to this carbocation. Use Nu:⁻ if you want to show a nucleophile and E^+ if you want to show an electrophile. Draw the structure of each product formed. Use curved arrows to show bonds breaking and forming.



3. (1 unit) SAM (S-adenosylmethionine) is formed from ATP and methionine in a substitution reaction. a. Circle the alpha carbon. Triangle the nucleophilic atom. Box the leaving group.



b. Draw the structure of the elimination product.

4. (2.5 units) 3-bromo-2,2-dimethyl butane reacts with each reagent shown below.

a. Draw the structure of the most probable substitution product, and most probable elimination product. <u>Note</u>: a reaction may not occur.

b. For each reaction, circle the major product (substitution or elimination).

Reagent

Substitution Product

Elimination Product

HCI

H₂O

5. (3 units) Organic chemistry involves the conversion of one functional group to another.

a. Identify Reagents A, B, C, and D.

b. Draw the structure of Compound 3.

c. When Compound 1 reacts with Reagent C, a racemic mixture of Compound 4 is produced. Compound 5 is an alkyl bromide. Draw the structure of Compound 5. Using curved arrows, show how Compound 5 is produced from Compound 1.

d. Compound 3 reacts with Compound 4. Draw the structure of the most probable substitution and elimination products.



Compound 4

Quiz 3

12/3/14

1. alkene addition and reverse (elimination). See structural features and intermediate. E.g., Give intermediate. Show two ways to make this intermediate.

2. alkyne pK and substitution reaction to lengthen chain

3. Alkyne addition – relate to alkene addition. See structural features.

1. a. Name one functional group that can be converted to an alkyne. Give a specific example of this reaction. Name the reaction type.

b. Name one way to form a carbon-carbon bond, i.e., lengthen a carbon chain. Give a specific example of this reaction. Name the reaction type.

2. a. Draw the structures of compounds A to D:



b. Use curved arrows to show how B is converted to C.

Chem 12A, FINAL EXAM - TAKE-HOME PART due Friday, December 12, 2014 at 11:30 am The Take Home Part of the Final Exam is worth 8% of your grade. 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. <u>You must do Question 4 on your own.</u> 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. (3.5 units) a. Organic reactions involve the conversion of one functional group to another. The functional group and structural features of an organic compound help you determine how the compound reacts. Fill in the blanks in Table 1. Each functional group should address each reaction type. Note: some functional groups will not undergo each reaction type.

Reactant Functional	Reaction Type	Structural Feature(s)	Product Functional	Example
Group			Group	
Alkene	Addition	Pi bond	RX, RX ₂ , ROH, RH,	
	Acid-base			
	Substitution			
	Elimination			
Alkyne	Addition			
	Acid-base			
	Substitution			
	Elimination			
Alkyl halide				
Alcohol				
Alkane				

Table 1. Reaction types, structural features, and products of each functional group.

b. The functional group and structural features of an organic compound help you determine how to prepare (synthesize) a compound. See Table 1. How is a product functional group reaction related to a reactant functional group reaction? c. Many organic reactions are reversible. For example, an alkene undergoes addition to form RX; RX undergoes elimination to form an alkene. Give other examples of CHM 12A functional group conversions that are reversible. State the reaction type for the forward and reverse reactions.

d. We looked at the following substances in CHM 12A this semester: H_2SO_4 , HBr, NaOH, NaHCO₃, Br₂, BH₃, NaOC₂H₅, 1pentene, 1-butanol, and water. Do the following: classify each substance as a nucleophile or electrophile. Rank the nucleophiles from strongest to weakest. Rank the electrophiles from strongest to weakest. For each reactant, state one reaction type that this reactant undergoes. Give one example of this reaction. Organize this information in a table. e. Determine the reaction conditions for each reaction. Be specific.



2. (2 units) You are about to do the following experimental procedure:

a. Add 0.35 ml of 1-hexene to a 15 ml reaction tube. Working in the hood, add 1.0 ml of 30% HBr in acetic acid (5 M) to the tube. Cap the tube and shake it frequently for 10 min. Occasionally loosen the cap to release any buildup of pressure. Describe the reaction that occurs. Draw the structure of reactants and products. What is the function of the acetic acid? b. After the reaction period, allow the phases to separate and remove the lower acetic acid layer ith a Pasteur pipet. Place the acid layer in a 150 ml beaker containing 50 ml of water. What substance is or is in the top layer? c. Add 2.0 ml of ether and 2.0 ml of water to the organic phase remaining in the reaction tube. Cap the tube and shake it to mix the phases. Separate the layers. Which layer, top or bottom, should you keep? Give reasons.

d. Wash the ether layer with 2.0ml of 5% sodium bicarbonate solution. Remove the lower aqueous phase. What does the sodium bicarbonate do? What observation tells you the sodium bicarbonate is working?

e. Add anhydrous calcium choloride pellets to the reminaing ether solution, and allow to dry for 10 minutes. What does the calcium chloride do?

f. If peroxides are present, will the same product as in part (a) form? Give reasons. Show the mechanism of this reaction. Use curved arrows to show bonds breaking and forming.

3. (2 units) Starting from acetylene, synthesize the following compounds. Use any necessary inorganic reagents. Synthesize any any organic reagents from acetylene.

a. 2,3-dibromobutane. Circle the chirality centers. Draw a Fischer projection of each stereoisomer of this compound. In each Fischer projection, determine the configuration at each chirality center. If there are more than two stereoisomers, identify the enantiomers, diastereomers, and meso compounds if any.
b. 4-methyl-2-pentene

4. (0.5 unit) 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. 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	Draw Lewis and skeletal structures of organic compounds	
2	Name and classify organic compounds by functional group; identify their physical and chemical properties, especially reactivity trends	
3	Identify common nucleophiles and electrophiles and be able to rank by strength	
4	Determine and compare stability, e.g., resonance, of organic compounds and apply to reactions	
5	Relate structure and reactivity to stereochemistry. Draw Newman and Fischer projections	
6	Apply (2), (3), (4), and (5) to predict products of organic reactions given reactants and reaction conditions given products	
7	Describe organic reaction mechanisms by type, identify common organic mechanistic processes, and use curved arrows to show bonds breaking and forming.	
8	Design syntheses of organic compounds	
9	Perform organic laboratory techniques to separate, isolate, and identify organic compounds	
10	Identify and distinguish between different characterization methods, e.g., IR, for organic compounds	
	Overall Chem 12A Grade	

c. Go to the Chem 12A Homework, Exams, and Old Exams web page and take the "Take Home Final Exam Question 4c" survey.

(i) How many questions were on the survey?

(ii) Briefly explain your answer to Question 4.

Name: _____

Chem 12A December 12, 2014

FINAL EXAM Show all work!! The Final Exam is worth 12% of your grade. You are allowed to use one 3"x5" card for notes. 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. Table 1. pK_a's of various acids.

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Acid	HBr	HCI	$(C_2H_5)_2OH^+$	$CH_3CH_2OH_2^+$	H₃O⁺	CH₃COOH	H ₂ O	CH ₃ CH ₂ OH	HC≡CH	NH ₃
рК _а	-6	-4	-3	-2	-1.7	4.8	15.7	16	25	35

1. (2.5 units) We studied the following functional groups in CHM 12A: alkanes, alkenes, alkynes, alkyl halides, and alcohols.

We identified the structural features in compounds, e.g., α carbon.

We classified polar organic chemical reactions as: acid-base, substitution, elimination, and addition.

We looked at the reaction mechanism for each reaction type.

a. Fill in the blanks in Table 1. In the "Functional group(s)" column, use the list of functional groups above.

Table 1. Summary of organic reaction types.

Reaction	Structural Feature(s)	Functional group(s)
type		
Acid-base	Acid: Acidic H, Base: lone pair on O	Alcohol, alkyne
Substitution		
Elimination		
Addition		

b. Substitution, elimination, and addition reactions involve the same type of intermediate.

(i) What type of intermediate is involved? Draw the structure of a three carbon organic compound of this intermediate.(ii) At what atom in the structure you drew in (i) does a substitution reaction occur? Circle this atom in your structure. Will a nucleophile or electrophile react with this atom?

(iii) At what atom in the structure you drew in (i) does an elimination reaction occur? Box this atom in your structure. Will a nucleophile or electrophile react with this atom?

(iv) Draw the structure of a reactant that undergoes an addition reaction that forms the intermediate you drew in (i).

c. H_2SO_4 , HBr, NaOH, NaHCO₃, Br₂, BH₃, NaOC₂H₅, 1-pentene, 1-butanol, and water are mixed together. Will a reaction occur? If so, which substances react and what are the products? (only one reaction occurs)

2. (4.5 units) Menthol (Compounds B) is found in peppermint, is an anesthetic and counterirritant, and is used to soothe throat irritation.

a. Determine the reaction conditions for (1) through (6). Draw the structures of E and F. You do <u>not</u> have to consider stereochemistry in your answers.



b. Which compound, A, B, C, or D, undergoes ozonolysis? Draw the structure of the product of this reaction. c. Describe how to synthesize menthol (Compound B) from Compound A.

3. (4 units) See the Reaction Map in Question 2.

a. Compound D reacts with Compound G. Two possible intermediates form.

(i) Use curved arrows to show how Compound D reacts with Compound G to form the each intermediate.

(ii) Which intermediate is more stable? Give reasons.

(iii) Use curved arrows to show how water reacts with each intermediate to form product(s). If more than one product forms, which product is the major product? Give reasons.

b. Compound C reacts with a nucleophile (Nu:). <u>Three</u> possible products form.

(i) Use curved arrows to show how Compound C reacts with Nu: to form each product.

(ii) If Nu: is H_2O , which product is the major product? Give reasons.

(iii) If Nu: is HC=C:, which product is the major product? Give reasons.

c. Compound D reacts with NBS/light in an allylic bromination reaction. How many allylic carbons are in Compound D? Draw the structure of the most likely product. Give reasons. (Hint: which radical is the most stable?)

4. (1 unit) a. Is menthol (shown below) optically active? If so, circle the chirality center(s) in the structure below. How many stereoisomers does menthol have?



b. In Question 2, Compound D reacts with Br₂ to form Compound E. Is Compound E optically active or an optically inactive racemic mixture? Give reasons.

c. Menthol (Compound B) reacts with Reagent (1) to form menthyl bromide (Compound C). What experimental evidence would you need to determine the mechanism (S_N 1 or S_N 2) of this reaction? Be specific.