

Name: \_\_\_\_\_

Chem 12B  
March 5, 2010

**Exam 1**  
show all work!!

Exam 1 is worth 10% of your grade (50 points). You are allowed to use one 8.5"x11" Periodic Table and 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. (10 points) a. Name and give the chemical formula of two oxidizing agents. Give one example of a Chem 12B reaction that uses this agent. Draw the structures of the reactants and products in your example.

b. Name and give the chemical formula of two reducing agents. For one of your reducing agents, identify the specific atom that reduces the organic compound. What is another name for this part? Give one example of a Chem 12B reaction that uses this agent. Draw the structures of the reactants and products in your example.

2. (8 points) In organic synthesis, a big organic molecule is synthesized from small organic starting materials.

a. Name and draw the structure of a common small organic starting material.

b. Name two methods covered in Chem 12B that are used to extend a carbon chain. For one method, identify the reaction type and give an example of a reaction. Draw the structures of the reactants and products in your example.

3. (6 points) Alcohols and ethers contain a C-O single bond.

a. Does the carbon behave like a nucleophile or electrophile? Give reasons.

b. What type of reaction can occur at this bond in alcohols and ethers?

c. How can the carbon be made into a better nucleophile or electrophile? Give reasons.

4. (6 points) Aldehydes, ketones, and acyl chlorides contain a C=O double bond (carbonyl group).

a. Does the carbonyl carbon behave like a nucleophile or electrophile? Give reasons.

b. What type of reaction can occur at this bond?

c. Of the three functional groups listed above, in which group is the carbonyl carbon most nucleophilic or electrophilic? Give reasons.

5. (20 points) A student dropped his lab notebook and many unattached IR and NMR spectra fell out. In reorganizing his notebook, he found a synthesis procedure and a MS, IR,  $^1\text{H}$  NMR, and  $^{13}\text{C}$  NMR spectra. The synthetic method is described as follows:

To  $\text{C}_3\text{H}_6$ , add  $\text{Br}_2/\text{H}_2\text{O}$ , followed by NaOH to form Compound A. To Compound A, add ethyl magnesium bromide followed by acid to form Compound B. Compound B is oxidized with  $\text{NaCr}_2\text{O}_7$  to form Compound C (the desired product).

a. Draw the structures of Compounds A, B, and C.

b. MS, IR,  $^{13}\text{C}$  NMR, and  $^1\text{H}$  NMR spectra are shown on the next page. Do the spectra match Compound C? Give reasons. (You do not have to use all of the spectral information if you don't need to.)

c. If your answer to part b is NO, describe a synthesis of the compound that matches the spectra. Use ethylene as your starting material. Use appropriate reagents as needed.

If your answer to part b is YES, describe an alternative synthesis of Compound C. Use ethylene as your starting material. Use appropriate reagents as needed.

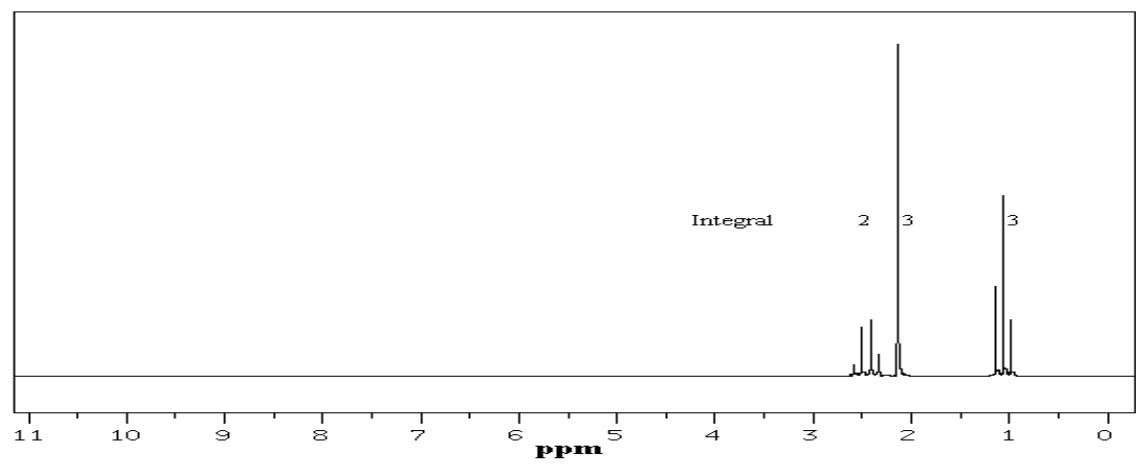
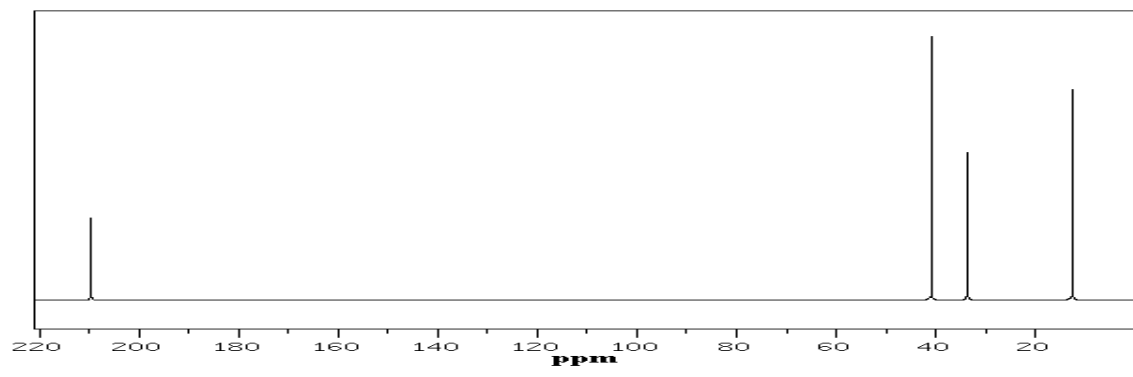
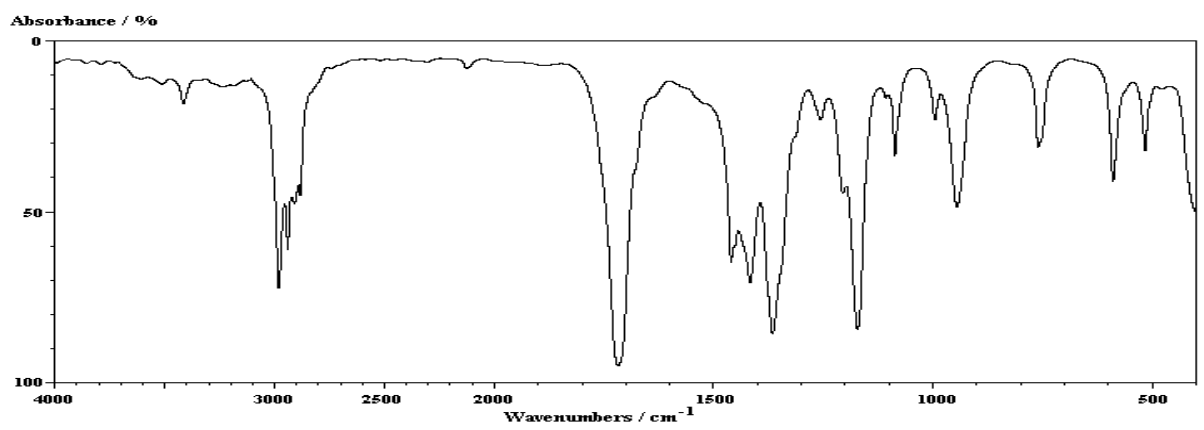
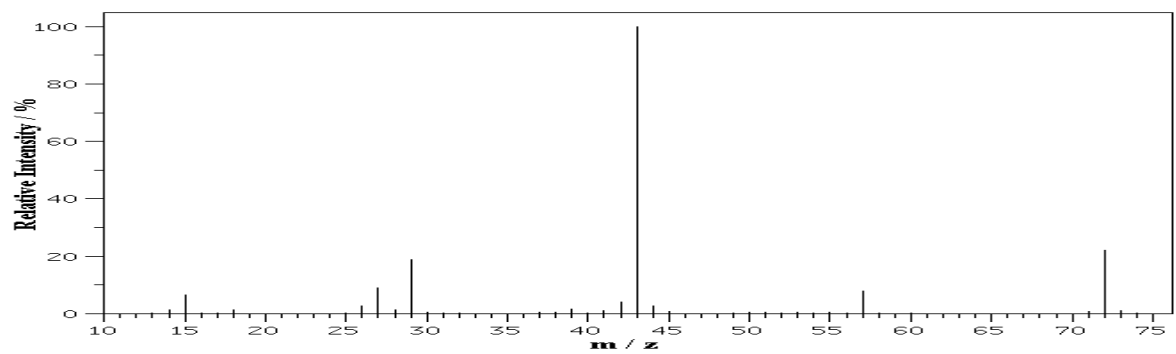


Table 1. IR correlation table (<http://www.chem.ucalgary.ca/courses/351/Carey5th/Ch13/ch13-ir-3.html>)

	Bond	Base Value	Strength / Shape	Comments
1	C=O	1715	s, "finger"	Exact position depends on type of carbonyl
2	O-H	3600	s, brd	Broad due to H bonding
3	N-H	3500	m	Can tell primary from secondary
4	C-O	1300-1000	s	Also check for OH and C=O
5	C=C	1650	w alkene m-s aromatic	Alkene w due to low polarity Aromatic usually in pairs
6	C-C	2150	w, sharp	Most obvious in terminal alkynes
7	C-H	3000	s	As hybridisation of C changes $sp^3$ - $sp^2$ - $sp$ , the frequency increases
8	C-N	2250	m, sharp	Characteristic since little else around it

Table 2.  $^1\text{H}$  NMR chemical shifts (<http://www.chem.ucalgary.ca/courses/351/Carey5th/Ch13/ch13-nmr-3b.html>)

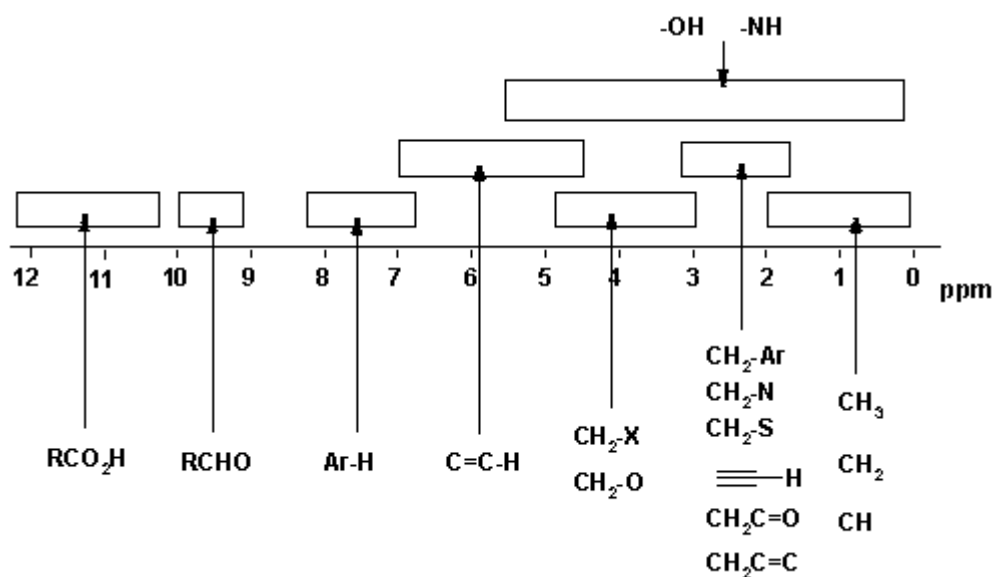
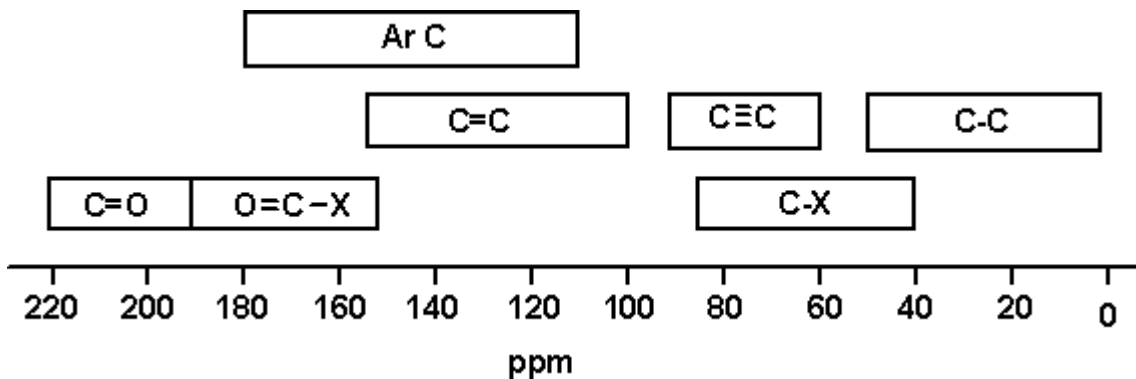


Table 3.  $^{13}\text{C}$  NMR chemical shifts (<http://www.chem.ucalgary.ca/courses/351/Carey5th/Ch13/ch13-cnmr-1.html>)



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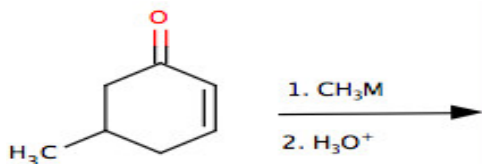
Chem 12B  
April 19, 2010

**Exam 2**  
show all work!!

Exam 2 is worth 10% of your grade (50 points). You are allowed to use one 8.5"x11" Periodic Table and 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. (5 points) Name one organic reaction covered in Chem 12B that is used to make a ring. Identify the reaction type or give the name of the reaction. Give a specific example of this reaction. Draw the structures of the reactants and products in your example.

2. (15 points) Consider the reaction of 5-methyl-2-cyclohexenone with an organometallic compound. M is either Li, MgBr, or CuLi.



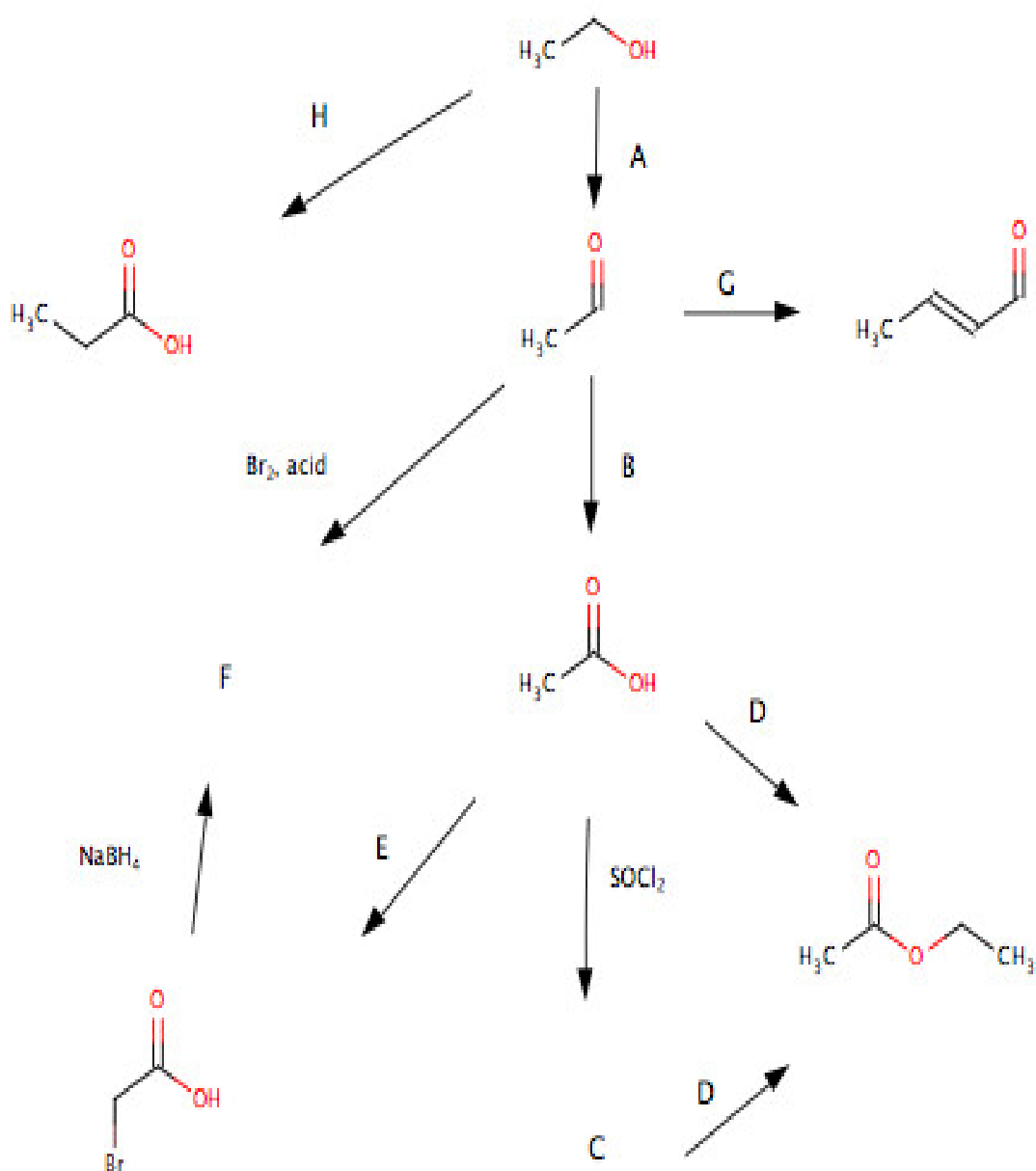
a. Identify the reactive site(s) in 5-methyl-2-cyclohexenone. State whether each site is a nucleophile or electrophile.

b. This reaction produces two possible products. Draw the structure of each product.

c. The table below shows the product distribution of the reaction of 5-methyl-2-cyclohexenone with three organometallic compounds. Explain the product distribution.

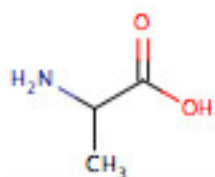
Nucleophile	1,2-Addition product	1,4-Addition product
CH <sub>3</sub> Li	>99%	<1%
CH <sub>3</sub> MgBr	79%	21%
(CH <sub>3</sub> ) <sub>2</sub> CuLi	2%	98%

3. (20 points) Draw the structure or identify the reaction conditions/synthesis steps for the letters A through H.



4. (10 points) In the Strecker synthesis of amino acids, an aldehyde reacts with ammonia to produce an imine. The imine then reacts with cyanide ion to form an  $\alpha$ -aminonitrile. Hydrolysis of the nitrile group yields the amino acid.

a. What aldehyde would you use to make glycine (shown below)? From this aldehyde, show the synthesis steps and intermediates to make glycine.



b. For the reaction of your aldehyde in part a to the imine, describe the reaction mechanism. For each step, identify the nucleophile and electrophile, use curved arrows to show bonds breaking and forming, and state the elemental mechanistic process.

**Chem 12B, FINAL EXAM - TAKE-HOME PART**  
due Friday, May 28, 2010 at 8 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 – 4 of the Final Exam. **You must do Question 5 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. (8 points) You synthesized mauve in Chem 12B lab by reacting aniline, o-toluidine, and p-toluidine in the presence of  $K_2Cr_2O_7$ .

a. Determine the mole ratio of aniline to o-toluidine to p-toluidine that you used in this reaction.

b. Mauve is a mixture of four related aromatic compounds, mauveine A, mauveine B, mauveine B2, and mauveine C. The structures are shown in the Mauveine entry in Wikipedia (<http://en.wikipedia.org/wiki/Mauveine>). Based on your answer in part a, which mauveine structure did you make in lab? Draw the structure of the mauveine compound. Circle the ring(s) that comes from aniline, o-toluidine, and p-toluidine.

c. Wikipedia has an article on phenazine (<http://en.wikipedia.org/wiki/Phenazine>). Phenazine is synthesized by reacting nitrobenzene with aniline. What type of reaction do you think this is? Give reasons. (Next time: ID the nucleophile and electrophile.)

2. (7 points) a. Find a biological or biochemical reaction in Chapters 25-28 that is related to a Chem 12B reaction. Explain why this reaction interests you.

**Note:** (i) If you work in a group of five or less, find two biological or biochemical reactions. Your two reactions should be from two different chapters.

(ii) If you work in a group of six or more, find three biological or biochemical reactions. Your three reactions should be from three different chapters.

b. Write a chemical equation and draw the structures of reactants and products that represents this biological or biochemical reaction. Cite the page number in Carey, "Organic Chemistry", 7<sup>th</sup> ed., 2008 where you found this reaction.

c. Describe how this reaction is related to a Chem 12B reaction. State the functional group(s) involved and the name of the reaction type.

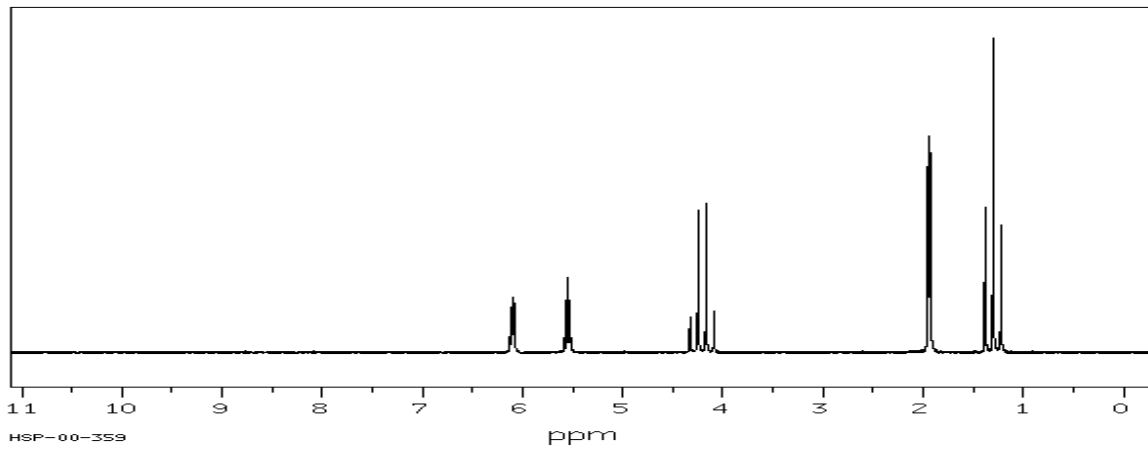
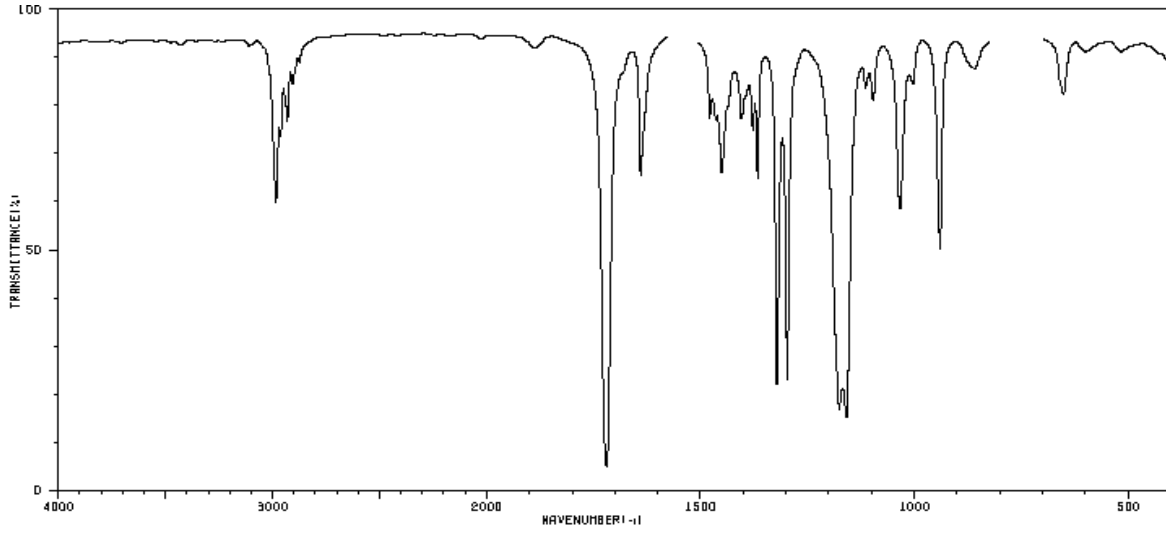
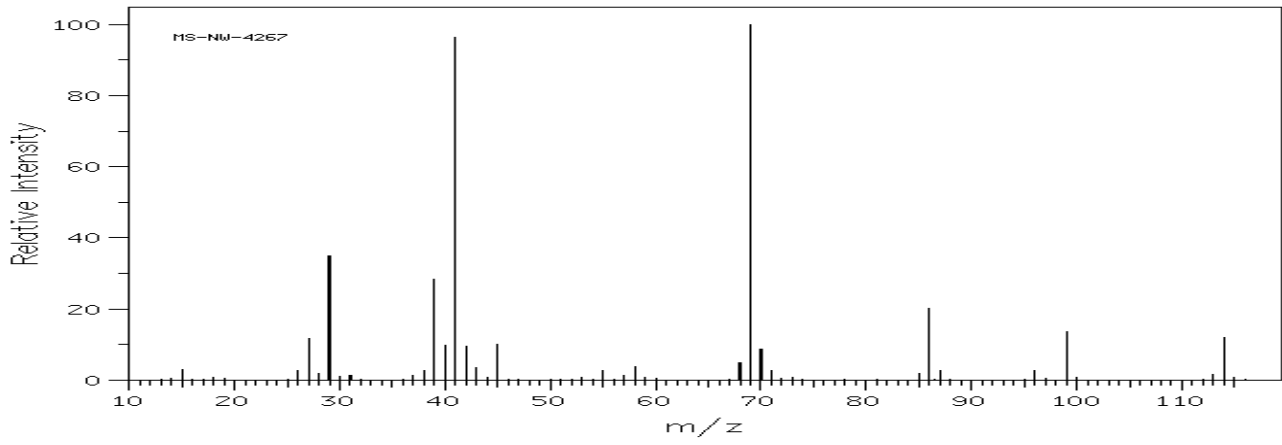
3. (15 points) In Quiz 9 on 5/5/10, capsaicin was synthesized from 6-methyl-4-heptenol (see Carey, "Organic Chemistry", 7<sup>th</sup> ed., p. 902, Problem 21.21).

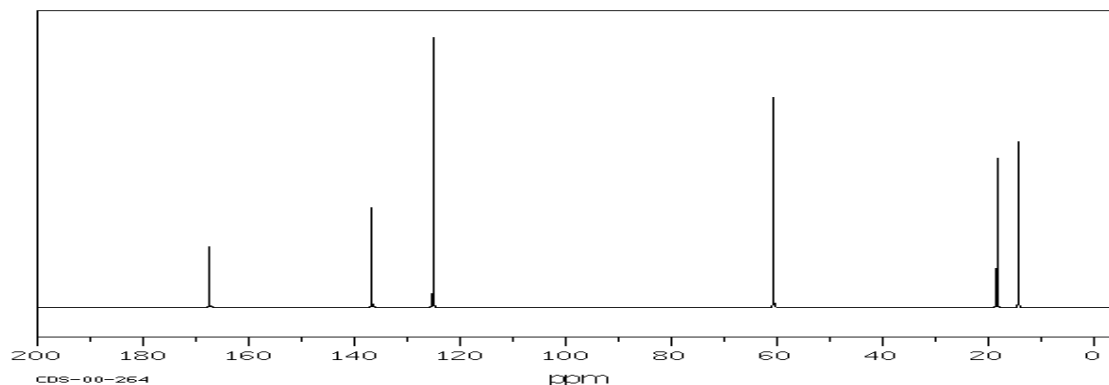
a. Starting from ethylene and using any necessary reagents, design a synthesis of 6-methyl-4-heptenol. (If your organic reagent contains more than two carbons, show a synthesis of this reagent starting from ethylene. If your organic reagent contains the benzene ring, show a synthesis of this reagent starting from benzene.)

b. Starting from ethylene and using any necessary reagents, design a synthesis of  $NaCH(CO_2CH_2CH_3)_2$ . (If your organic reagent contains more than two carbons, show a synthesis of this reagent starting from ethylene. If your organic reagent contains the benzene ring, show a synthesis of this reagent starting from benzene.)

c. Starting from benzene and using any necessary reagents, design a synthesis of 2-methoxy-4-methylaminophenol. (If your organic reagent contains more than two carbons, show a synthesis of this reagent starting from ethylene. If your organic reagent contains the benzene ring, show a synthesis of this reagent starting from benzene.)

4. (10 points) Ethyl propanoate is treated with LDA to make Compound A. Compound A is treated with formaldehyde and heat to make Compound B. IR, NMR, and MS spectra for Compound B are shown below. Draw the structures of Compounds A and B. Describe your analysis of each spectrum for full credit.





5. (10 points) According to the Chem 12B Course Information Handout, your “grade will be based on your performance and mastery of the last Course Objective.” Each course objective is shown below.

- 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
- Identify the course objective that you understand the best. What did you do to help you understand this objective so well?
- Identify the course objective that you understand the worst. What could you have done to understand this objective better?
- Give yourself an overall course grade based on your understanding of the course objectives. Objectives 6, 7, and 10 are the most important 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	relate the name of organic compounds to structure and vice versa	
2	relate the structure, bonding, and geometry of a compound to its reactivity	
3	identify common nucleophiles and electrophiles	
4	identify common organic mechanistic processes in a reaction mechanism and the use of curved arrows	
5	understand reactivity principles and trends (see handout)	
6	apply and relate (3), (4), and (5) to predict conditions and products of organic reactions, e.g., the conversion of one functional group to another	
7	design syntheses of organic compounds	
8	identify and distinguish between different characterization methods for organic compounds	
9	interpret IR spectra, NMR spectra, and MS to determine the structure of an organic compound	
10	perform organic laboratory techniques	
	<b>Overall Chem 12B Grade</b>	

Name: \_\_\_\_\_

Chem 12B  
May 28, 2010

**Final Exam**  
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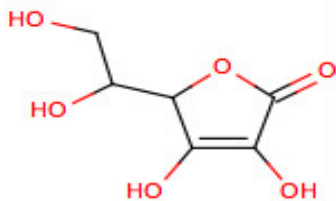
- (12 points)
  - Give an example of one reaction covered in Chem 12B that is used to increase the length of a carbon chain (forms a C-C bond). Identify the reaction type. Draw the structures of the reactants and products in your example.
  - Give an example of one reaction covered in Chem 12B that is used to decrease the length of a carbon chain. Identify the reaction type. Draw the structures of the reactants and products in your example.
  - Give an example of one reaction covered in Chem 12B that is used to make a ring. Identify the reaction type. Draw the structures of the reactants and products in your example.

- (8 points) a. State the function of each reagent/reaction condition.

Reagent/reaction condition	Function
$K_2Cr_2O_7$	
LDA	
(i) $LiAlH_4$ in ether, (ii) $H_2O$ & base	
KOH in $H_2O$	
$NaNO_2$	
$Br_2$ /acetic acid	

- Dustin Haddenham from UCSC gave a talk (5/21/10) on "Methodology Development within Organic Chemistry: Reactions of the Fifth Element". What reagent in part a could be substituted for lithium aminoborohydride? Give reasons.

- (14 points) Vitamin C is also called ascorbic acid.



- What type of ring is contained in Vitamin C? What type of carbonyl group is in Vitamin C? What type of alkene is in Vitamin C?
  - Vitamin C has several acidic protons. See the OH groups on the  $\alpha$ -carbon and  $\beta$ -carbon. Draw the structure of the conjugate base of Vitamin C when the OH hydrogen is removed from the  $\alpha$ -carbon. Draw the structure of the conjugate base of Vitamin C when the OH hydrogen is removed from the  $\beta$ -carbon. Which H do you think is more acidic? Give reasons. (Hint: consider resonance structures.)
  - When Vitamin C is ingested into the acidic environment of the stomach, a hydrolysis reaction occurs. Draw the structure of the hydrolysis product.
  - Describe a mechanism for the hydrolysis reaction in part c. For each step, identify the nucleophile and electrophile, use curved arrows to show bonds breaking and forming, and state the elemental mechanistic process.
- (16 points) Letters A through I represent a structure or reaction condition(s)/synthesis step(s). Complete 8 out of 10 of the letters. If you complete 8 correctly, each additional correct answer is 1 point extra credit.