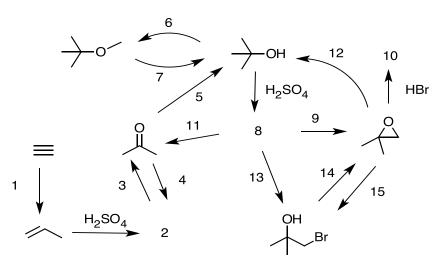
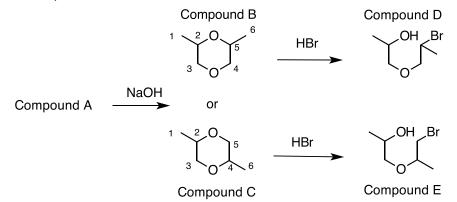
Exam 1

show all work!!

Exam 1 is worth 10% of your grade. You are allowed to use one $3^{\circ} \times 5^{\circ}$ 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 1 unit. 1. (8 units) Identify the reaction conditions or draw the structure for (1) through (15).



2. (10 units) Compound A (C_3H_7BrO) is treated with NaOH to make $C_6H_{12}O_2$. The structure of $C_6H_{12}O_2$ is either Compound B or Compound C. Compound B is treated with 1 equivalent of HBr to produce Compound D. Compound C is treated with 1 equivalent of HBr to produce Compound E. When Compound D <u>or</u> Compound E is treated with excess HBr, Compound A is produced.



a. Show the reaction mechanism of the reaction of Compound B + HBr \rightarrow Compound D. Use curved arrows to show bonds breaking/forming in each step. Draw the structure of each intermediate.

b. What does the ¹H nmr spectrum of Compound B and Compound C look like? Fill in the Table 1. Determine the number of peaks (signals). You do not have to determine the chemical shift. For each peak, identify the carbon(s) on which each H is equivalent, state the # of equivalent H's, and the splitting (singlet, doublet, etc.). If a peak is coupled to two different types of H's to produce a complex splitting pattern, state the splitting to each different H, e.g., singlet and doublet. For example, one peak is due to the H's bonded to C-1 and C-6 with 6 equivalent H's, and will be split into a doublet.

Compound B					Compo	Compound C				
Peak	Carbon #	# of equivalent H's	Splitting		Peak	Carbon #	# of equivalent H's	Splitting		
1	C-1, C-6	6	doublet		1					
2	C-2, C-5	2	Triplet,							
			quartet							

Table 1. ¹H nmr interpretation of Compounds B and C.

3				

c. Can you use ¹H nmr be used to distinguish between Compounds B and C?

d. What does the ¹H nmr spectrum of Compound D and Compound E look like? Fill in the Table 2. Determine the number of peaks (signals). You do not have to determine the chemical shift. For each peak, identify the carbon(s) on which each H is equivalent, state the # of equivalent H's, and the splitting (singlet, doublet, etc.). If a peak is coupled to two different types of H's to produce a complex splitting pattern, state the splitting to each different H, e.g., singlet and doublet.

Table 2. ¹H nmr interpretation of Compounds D and E.

Compo	ound D			Compound E					
Peak	Carbon #	# of equivalent H's	Splitting		Peak	Carbon #	# of equivalent H's	Splitting	
1					1				
2					2				
3					3				

e. Can you use ¹H nmr be used to distinguish between Compounds D and E?

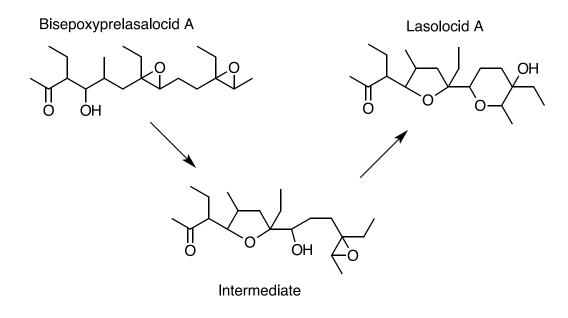
f. Draw the structure of Compound A.

3. (3 units) a. Propose a plausible synthesis.

≠ ____ \ Å

4. (4 units) Bisepoxyprelasalocid A is treated with a base to produce the antibiotic, Lasolocid A.

a. Describe the mechanism of this reaction Use curved arrows to show bonds breaking and forming.

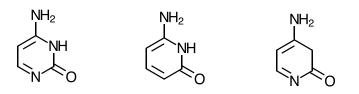


b. Based on ring opening epoxide reactions, is the intermediate shown the expected intermediate? Give reasons.

Exam 2

show all work!!

Exam 2 is worth 10% of your grade. You are allowed to use one 3" x 5" 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 1 unit. 1. (2 units) a. DNA bases are aromatic. Identify the aromatic compound. Give reasons for your choice.

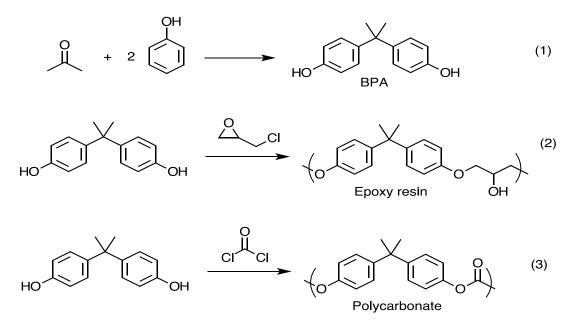


b. Alkenes undergo electrophilic addition whereas aromatics undergo electrophilic aromatic subsitution. Show the mechanism of the reaction of benzene with a generic electrophile, E⁺. Use curved arrows to show bonds breaking and forming. Explain why benzene undergoes electrophilic aromatic subsitution and not electrophilic addition.

2. (1.5 points) The compound below is treated with HBr. Draw the structures of the possible products. At least three products are formed. Determine the product that is formed in the highest amount. Give reasons for your choice.

HBr

3. (1 unit) Bisphenol A (BPA) is the starting material to make polycarbonate plastics (CEN, 6/6/11, p. 14-19) but is no longer used in plastic bottles because it is an endocrine disruptor.



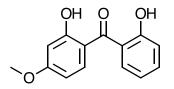
a. BPA is made from acetone and phenol. In Reaction (1), circle the carbon in BPA that came from the carbonyl carbon in acetone.

b. Is Reaction (1) a proton transfer, electrophilic addition, nucleophilic addition, electrophilic aromatic substitution, or elimination reaction?

c. In Reaction (2), box the carbon in Epoxy resin that came from the less substituted carbon in the epoxide.

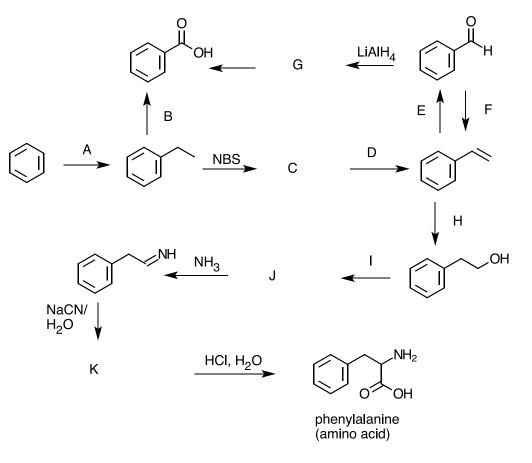
d. In Reaction (3), triangle the carbon in Polycarbonate that came from the carbonyl carbon in COCl₂.

4. (1.5 unit) Dioxybenzone (shown below) is a FDA approved sunscreen ingredient that is insoluble in water. Propose an efficient synthesis of dixoybenzone from phenol, m-methoxyphenol, any organic compound of three carbons or less, and any necessary inorganic reagents.



5. (4 units) Phenylalanine, an amino acid, is synthesized from benzene.

a. Draw the structure or identify the reaction conditions for A through K. (Note: $-C=N + H^+/H_2O \rightarrow -COOH$ for K \rightarrow phenylalanine)



b. Phenylalanine is treated with Br₂/FeBr₃. Draw the structure of the product of this reaction.

c. Phenylalanine is treated with acetone. Draw the structure of the product of this reaction.

Chem 12B, FINAL EXAM - TAKE-HOME PART

due Friday, May 24, 2012 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 a group with other students 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. (3 units) a. Table 1 shows the functional groups and reaction types we covered in Chem 12B. Functional groups undergo different reaction types.

(i) Check the box for the reaction type(s) for each functional group. (Note: focus on reactions we covered in lecture and lab. We did not cover reactions, such as the Birch reduction and Wittig reaction.)

Table 1 Reaction types in functional groups

rable 1. Neaction types in functional groups.								
Functional	H ⁺ transfer	Substitution	Elimination	Addition	Oxidation	Reduction		
Group								
ROH								
ROR								
Aromatic								
RCHO/RCOR								
RCOOH								
RCOOR								
RCOCI								
RCONH ₂								
Enolate								
RNH ₂								

(ii) For **one** reaction type for **each** functional group, give one sample reaction. Show the reactant(s) and product(s) and any necessary reagent(s).

b. A functional group reacts with another functional group to form a new functional group. Table 2 shows a matrix of functional groups. If a reaction occurs between two functional groups, write the name of the group that is formed in the box. E.g., ROH reacts with RCHO to form an hemiacetal/acetal.

Table 2. Functional group reaction matrix.

	ROR	Benzene	RCHO/ RCOR	RCOOH	RCOOR	RCOCI	RCONH ₂	enolate	RNH ₂
ROH			Hemiacetal/ acetal						
ROR	Х								
Ben-zene	Х	Х							
RCHO/ RCOR	Х	X	X						
RCOOH	Х	Х	Х	Х					
RCOOR	Х	Х	Х	Х	Х				
RCOCI	Х	Х	Х	Х	Х	Х			
RCONH ₂	Х	Х	Х	Х	Х	Х	Х		
Enolate	Х	Х	Х	Х	Х	Х	Х	Х	

c. A reagent gives you clues to reaction type and functional group. For each reagent below, give one example of a reaction that uses this reagent. Give the reactants and products.

b. NBS

c. LiAlH₄

d. LDA

e. SOCl₂

f. KMnO₄

g. O₃

h. RCOOOH

a. AICl₃

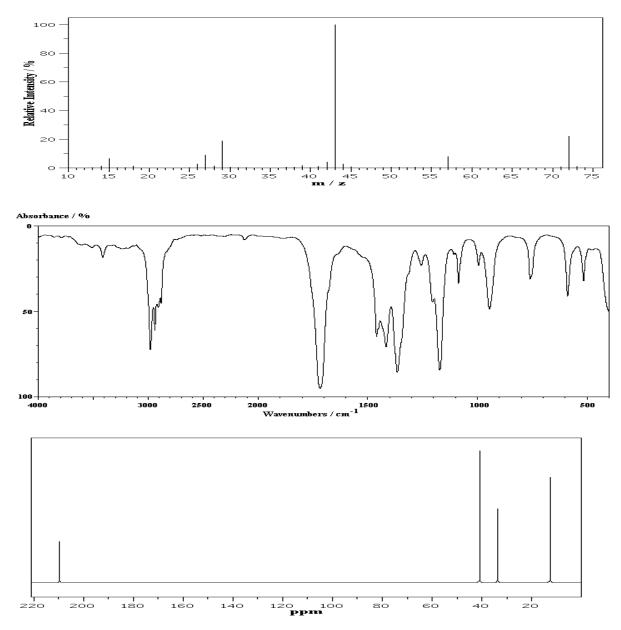
2. (2 units) A student dropped his lab notebook and many unattached IR and NMR spectra fell out. In reorganizing his notebook, he found a synthesis procedure and a MS, IR, ¹H NMR, and ¹³C NMR spectra. The synthetic method is described as follows:

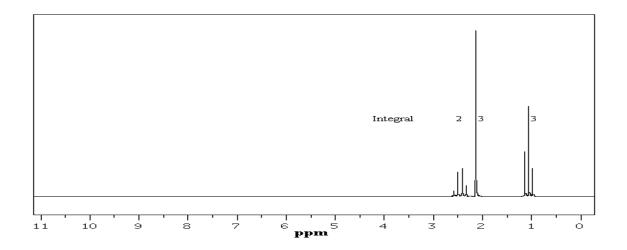
To C_3H_6 , add Br_2/H_2O , followed by NaOH to form Compound A. To Compound A, add ethyl magnesium bromide followed by acid to form Compound B. Compound B is oxidized with $Na_2Cr_2O_7$ to form Compound C (the desired product). a. Draw the structures of Compounds A, B, and C.

b. MS, IR, ¹³C NMR, and ¹H 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.)

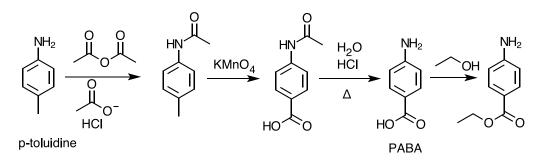
c. If your answer to part b is NO, describe a synthesis of the compound that matches the spectra. Use ethylene as your starting material. Use appropriate reagents as needed.

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.





3. (2 units) p-amino benzoic acid (PABA) is a sunscreen ingredient. PABA is synthesized from p-toluidine in three steps. The last step of this sequence involves the synthesis of a PABA derivative. (In the old days, compounds were characterized by making chemical derivatives.) Show the mechanism of Steps 1, 3, and 4. (Skip the KMnO₄ step.) Use curved arrows to show bonds breaking and forming. Draw the structures of intermediates as needed.



4. (1 unit) 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.

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. 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	
	Overall Chem 12B Grade	

c. Go to the Chem 12B 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) Which question on the survey was the hardest question to answer?

Survey: strongly disagree, disagree, neutral, agree, strongly agree

- The block schedule of lecture and lab (two 1.5 hour lectures followed by lab on the same day) was: made for a long, tiring day, helped me understand CHM 12B, made it hard to study between Wednesday and the following Monday, allowed me to get to know my classmates better
- 2. I was able to study 6 hours per week for CHM 12B.
- 3. I learned organic chemistry best from: lecture, lab, self, textbook, instructor studying with other students.
- 4. I prefer lectures in which the instructor lectures rather than practicing organic reactions.
- 5. The online homework forced me to read the textbook.
- 6. The quizzes forced me to do the practice problems from the textbook.
- 7. I learned CHM 12B better by studying with other students than by myself.
- 8. Having to work with other students in lecture and turn in my work did not help me learn organic chemistry.
- 9. The problem solving skills and critical thinking skills I learned in this course will help me in future courses.
- 10. I would rather pay for an organic chemistry lab textbook than have free experiments posted on the Chem 12B web site.
- 11. After two semesters of organic chemistry, I recognize functional groups, I have a good idea of how organic compounds react, I tried to memorize every #*?% reaction, still seems like a foreign language to me, organic chemistry sucks
- 12. The best thing about CHM 12B is:
- 13. The worst thing about CHM 12B is:

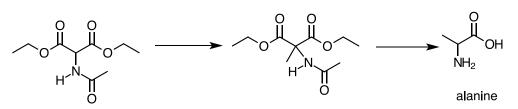
Final Exam

show all work!!

The In-Class part of the Final Exam is worth 12% of your grade. You are allowed to use one 3"x5" note card. Show all work for full credit. Write your answers legibly. You may ask me for a hint; however, each hint will cost you 0.5 units 1. (3 units) Based on the reactions we covered in CHM 12B this semester, describe two reaction(s) that make a C-C bond. Give one example of each reaction.

b. Based on the reactions we covered in CHM 12B this semester, describe two reaction(s) that break a C-C bond. Give one example of each reaction.

c. The amidomalonate synthesis is one way to synthesize amino acids, such as alanine. Determine the reaction conditions for each step.



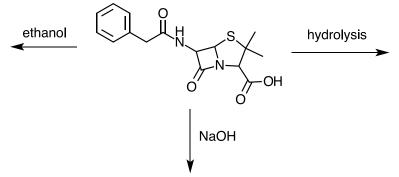
diethyl acetamidomalonate

2. (2 units) Penicillin G (below) is an antibiotic.

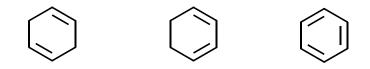
a. Under the conditions of our stomach, Penicillin G undergoes hydrolysis. Draw the structure(s) of the metabolic products of this hydrolysis reaction.

b. Penicillin G is treated with ethanol. At what atom in Penicillin G would you predict the ethanol would react? Give reasons and draw the product of this reaction.

c. Penicillin G is treated with NaOH. At what atom in Penicillin G would you predict the NaOH would react? Give reasons and draw the product of this reaction.



3. (4 units) a. You have several gallons of each of the compounds shown below that are stored in the chemistry stockroom.

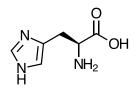


(i) Rank the following in order of reactivity (most reactive to least reactive).

(ii) You find a bottle of HBr stored next to one of the compounds from part (i). You think, "Is it safe to have HCl next to this compound?" You conclude these two compounds are probably ok next to each other. Which compound is it? Give reasons.

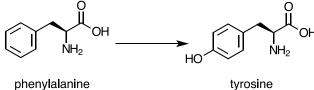
(iii) Which compound reacts with a peroxyacid? Give reasons.

b. (i) Histidine is an amino acid. Is histidine aromatic? Give reasons.



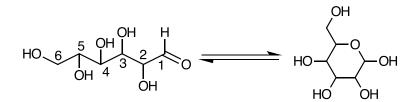
(ii) Histidine has two pi bonds. At which pi bond will an electrophile (E^+) react? Draw the structure(s) of the intermediate(s) and give reasons based on stability.

c. Phenylalanine is an amino acid. At which position in the ring will phenylalanine undergo electrophilic aromatic substitution? Give reasons.



The enzyme phenylalanine hydrolase converts phenylalanine to the amino acid tyrosine. Suggest an efficient synthesis of tyrosine from phenylalanine.

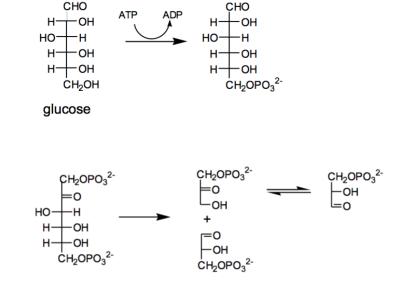
4. (3 units) Glucose, $C_6H_{12}O_6$, exists as an open chain or a pyranose ring (6 membered ring with five carbons and one oxygen). Each carbon in the open chain structure is numbered 1 through 6.



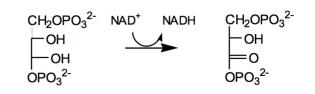
a. Label each carbon in the ring form of glucose with a number 1 through 6. Each carbon number in the ring form of glucose should match the carbon number on the chain form.

b. Show the mechanism of this reaction. Use curved arrows to show bonds breaking and forming. Draw the structures of the intermediates.

c. In glycolysis, glucose is converted to pyruvate in a 10 step reaction sequence. Three steps of glycolysis are shown below. For each step, identify the reaction type (H^{+} transfer, addition, elimination, substitution, oxidation, reduction). (i)



(ii)



(iii)