



Chem 342 • Organic Chemistry II

Exam 01 • 13 February 2009

KEY

Great events in Chemistry...



1865: Kekulé, moments before his brilliant insight into the structure of benzene.

Please read through each question carefully and answer in the spaces provided.

A good strategy is to go through the test and answer all the questions you can do easily. Then go back and tackle the more difficult problems.

Please make sure your structures are drawn clearly and indicate any stereochemistry with bold or dashed bonds.

Finally, think about what you know. Reason and common sense can often help you out.

Problem 1 12 pts _____

Problem 2 6 pts _____

Problem 3 10 pts _____

Problem 4 6 pts _____

Problem 5 12 pts _____

Problem 6 18 pts _____

Problem 7 12 pts _____

Problem 8 6 pts _____

Problem 9 5 pts _____

Problem 10 13 pts _____

TOTAL 100 pts _____

1. Indicate whether the following statements are True or False. (12 pts)

F A more conjugated molecule will absorb light at a shorter wavelength than a less conjugated molecule.

F Chlorobenzene reacts faster than benzene toward electrophilic aromatic substitution.

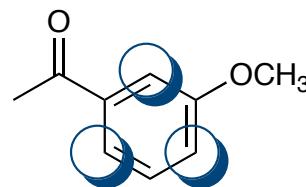
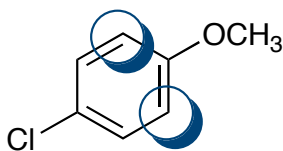
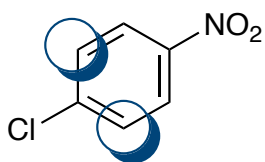
F The Diels Alder Reaction takes place in two steps.

F In ^{13}C NMR, the size of the peaks is exactly related to the number of hydrogens attached.

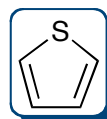
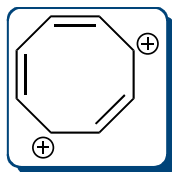
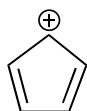
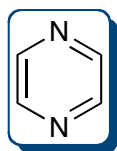
F In a kinetically controlled reaction the major product is the one that is lowest in energy.

F A CH_2 group will split into three peaks if it is next to a CH_3 group.

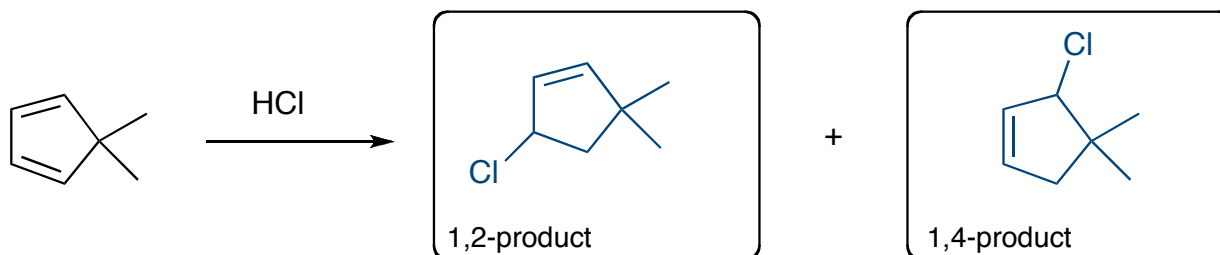
2. For each of the following molecules, indicate which position on the ring would electrophilic aromatic substitution would preferentially take place (circle the specific carbon). (6 pts)



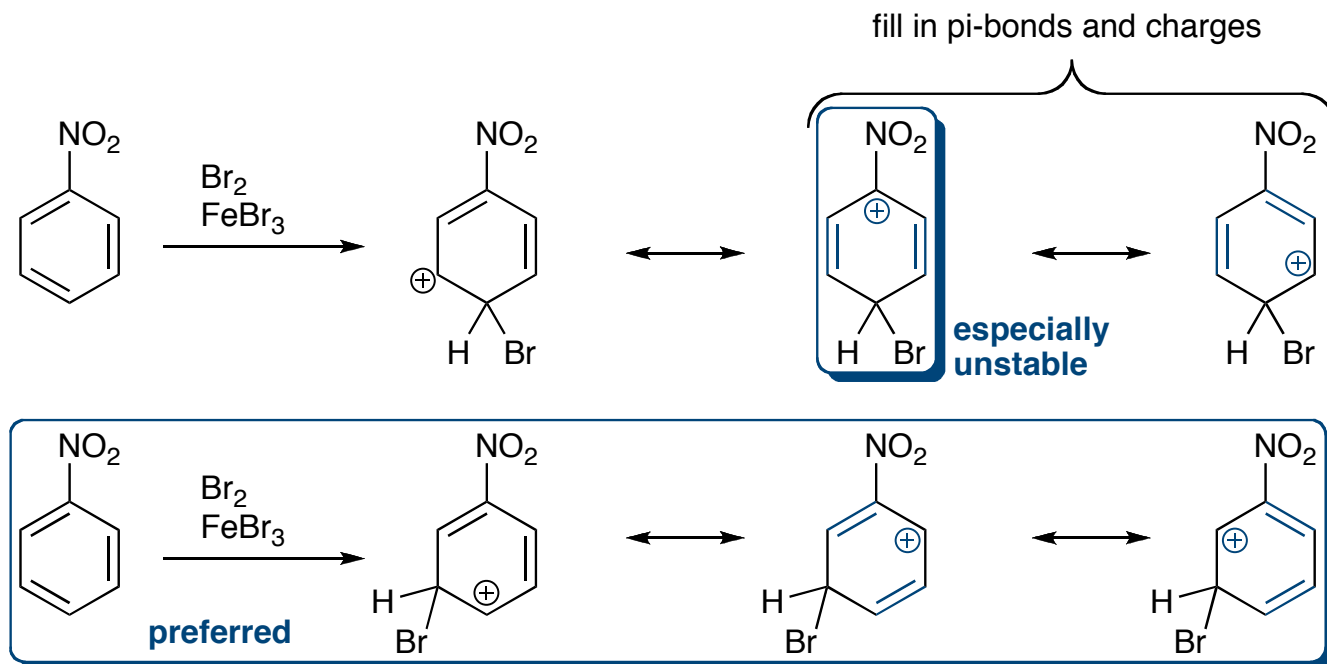
3. Circle all of the following molecules that are aromatic. (10 pts)



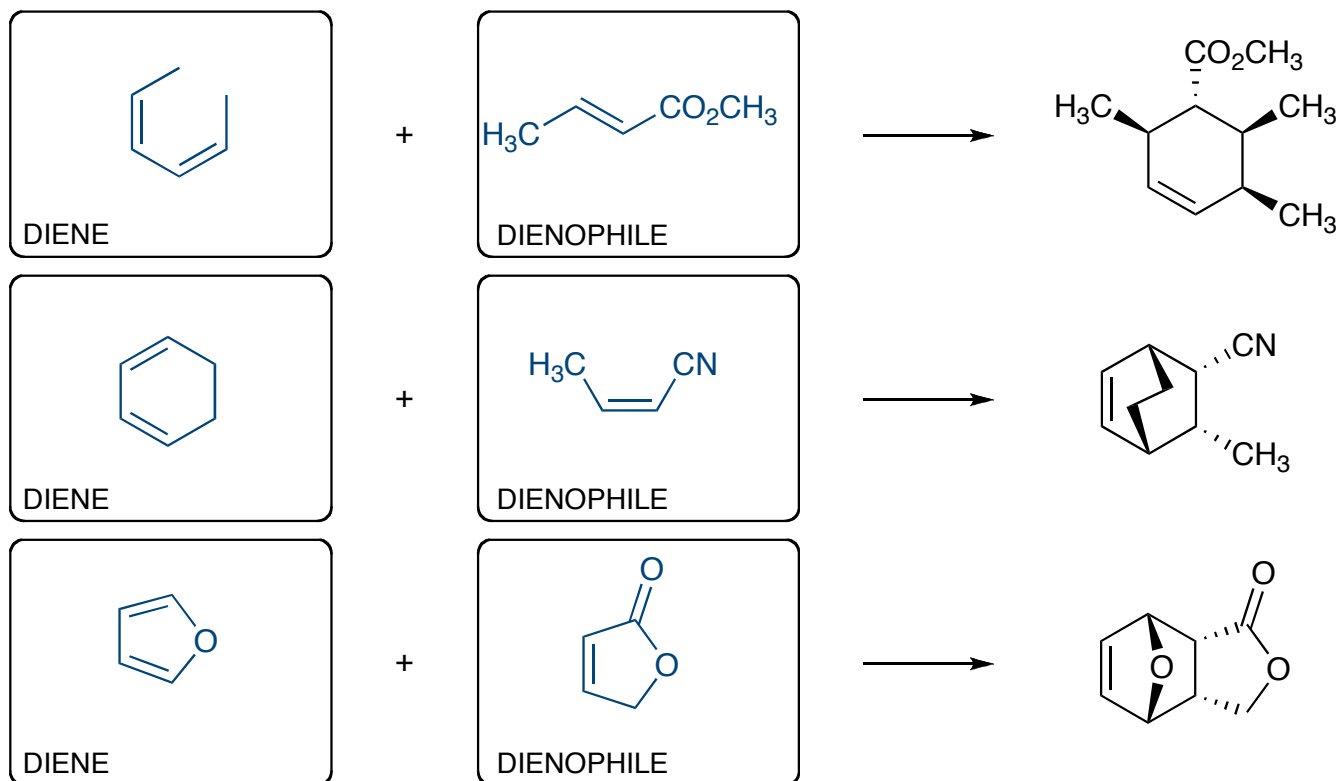
4. Draw the 1,2- and 1,4-products for the reaction of HCl with the following diene. (6 pts)



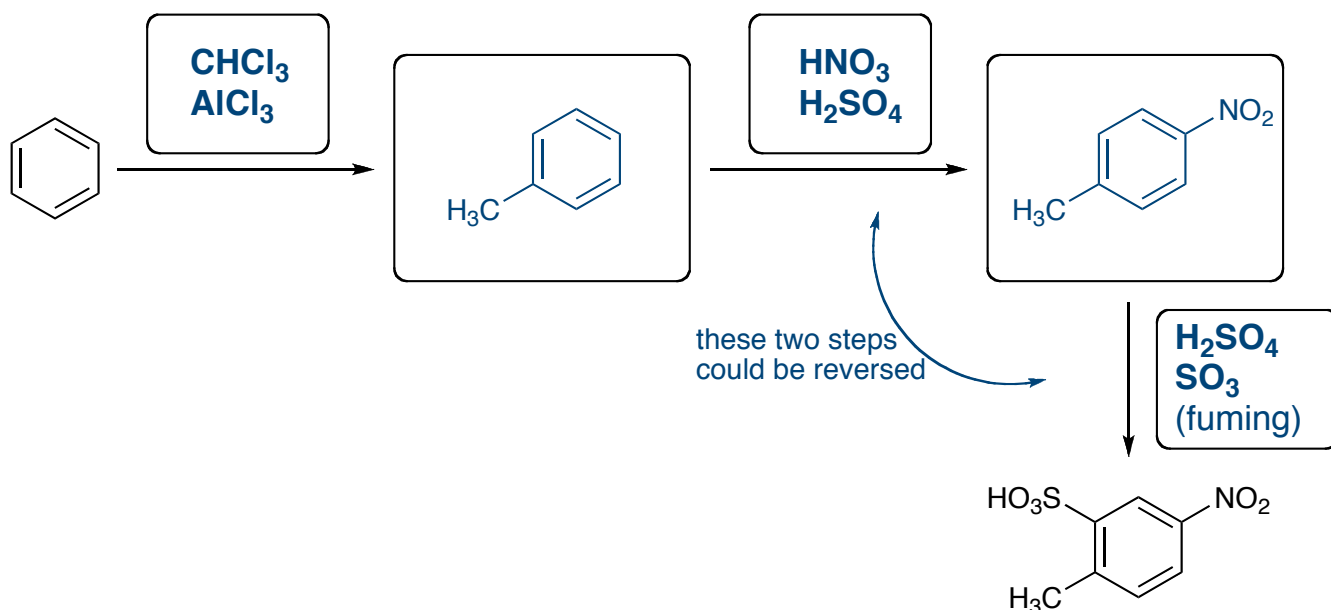
5. The first step of the electrophilic bromination of nitrobenzene is shown below for both addition to the para and meta positions. The first intermediate structure is drawn for you completely. Fill in all the missing pi-bonds and charges in the remaining intermediate resonance forms. Circle the least stable structure. Indicate which pathway would be the preferred reaction. (12 pts)



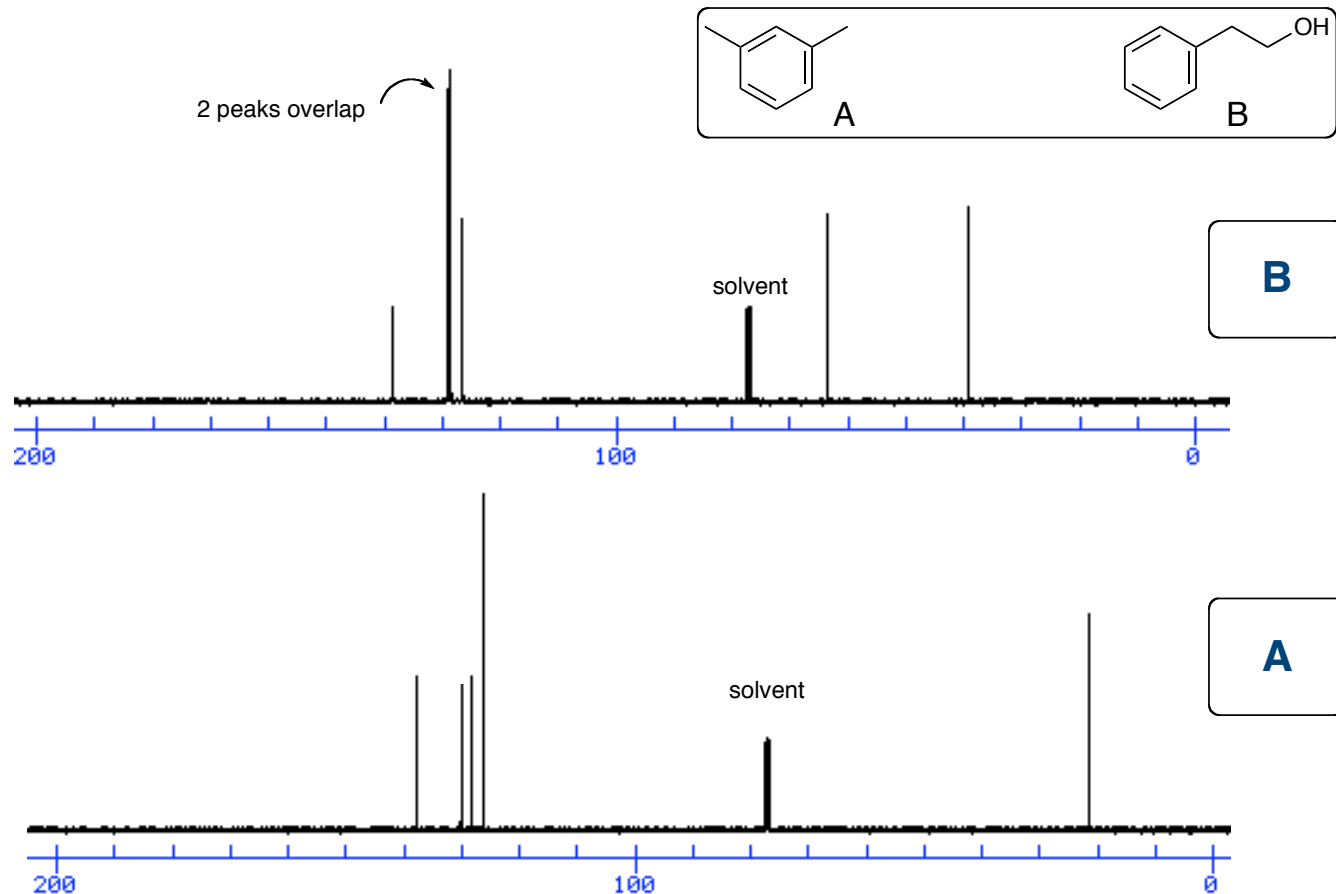
6. Draw the structures for the diene and the dienophile that were reacted to form the following products of the Diels-Alder reaction. (18 pts)



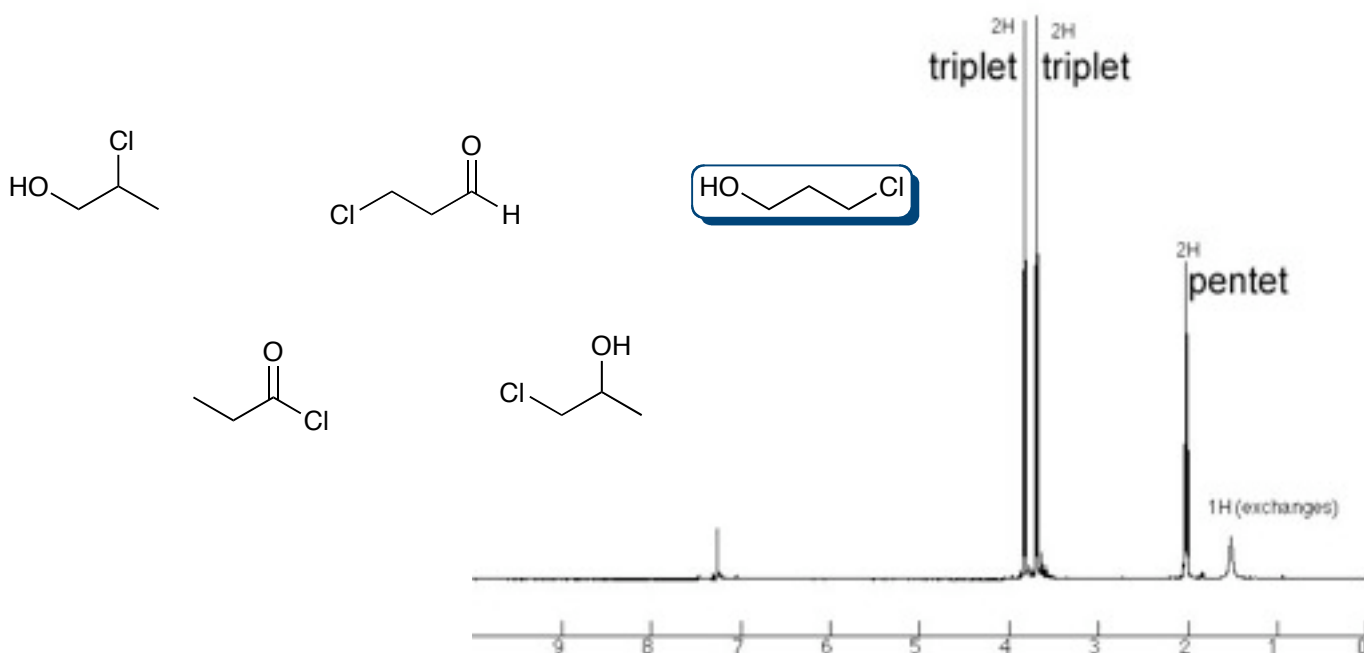
7. Starting from benzene, show how you would carry out the three step synthesis of the product shown. Fill in the reagents necessary for doing each of the three steps; Friedel-Crafts methylation, sulfonation, and nitration. Draw the intermediate structures. Pay attention to the order of reactions as it will affect the successful placement of all three substituents. (12 pts)



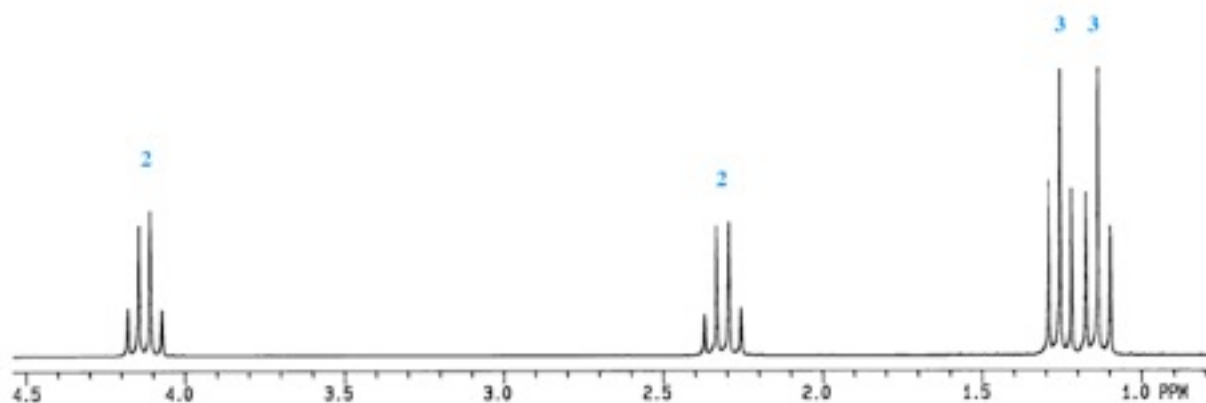
8. The ^{13}C spectra for two molecules are shown below. Match the molecule with the correct spectra by writing the letter in the box. (6 pts)



9. Circle the structure that best correlates with the following ^1H NMR spectrum. The peak at 7.2 ppm is from the solvent. (5 pts)



10. The proton NMR spectrum of an unknown compound with the molecular formula $\text{C}_5\text{H}_{10}\text{O}_2$ is shown below. In addition to the proton NMR the compound shows five peaks on the ^{13}C NMR at 174, 61, 27, 14, and 9 ppm.



- a) How many units of unsaturation are present? (3 pts)

1

- b) Which resonance on the proton NMR corresponds to a CH_2 group directly attached to an oxygen (circle one)? (3 pts)

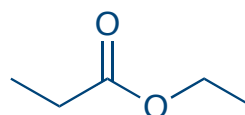
4.12 ppm

2.31 ppm

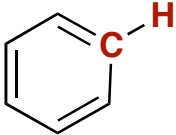
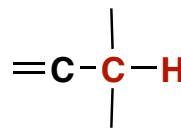
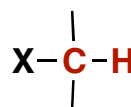
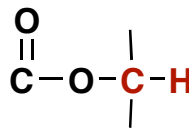
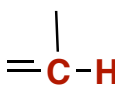
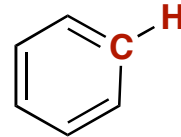
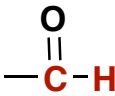

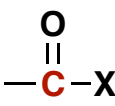
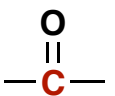
1.25 ppm

1.15 ppm

- c) Draw the structure for this molecule. (7 pts)



Typical NMR Chemical Shifts

Functional Group	Type	¹ H Chemical Shift (ppm)	¹³ C Chemical Shift (ppm)
	Alkane	0.7 - 1.8	10 - 60
	Allylic or next to carbonyl	1.6 - 2.4	30 - 60
	next to halogen or alcohol	2.5 - 4.0	20 - 85
	next to oxygen of an ester	4.0 - 5.0	50 - 85
	vinyl	4.5 - 6.5	110 - 150
	aromatic	6.5 - 8.0	110 - 140
	aldehyde	9.7 - 10.0	190 - 220
	alcohol	varies widely will exchange with D ₂ O	N/A
	carbonyl of ester, amide, or carboxylic acid (X = O, N)	N/A	165 - 185
	carbonyl of ketone or aldehyde	N/A	190 - 220