

## Chemistry 334R

### Problem Set 10

1. Circle the number that corresponds to the correct answer for each of the following four questions.

A. Which of the following carbonyl compounds reacts most readily with nucleophiles?

1. pentanoyl chloride
2. (*S*)-3-methylpentanamide
3. methyl pentanoate

B. Which reagent reacts with carboxylic acids to form the corresponding methyl esters?

1. diazomethane
2. methyllithium
3. both

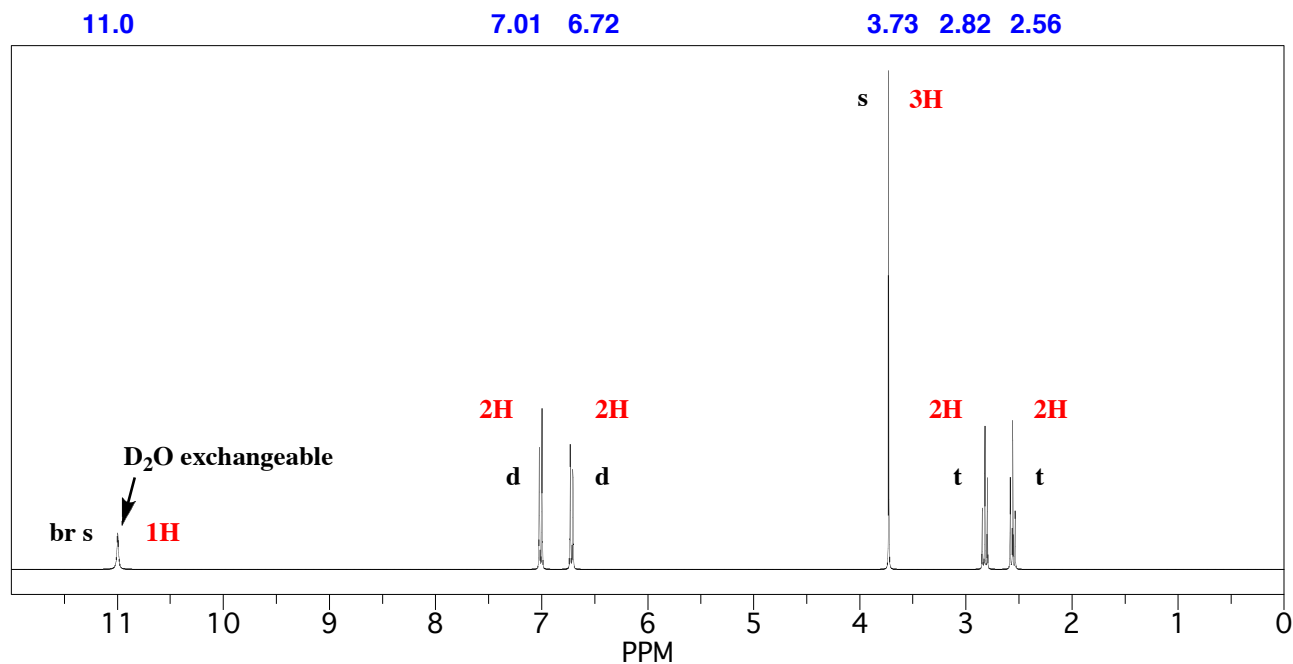
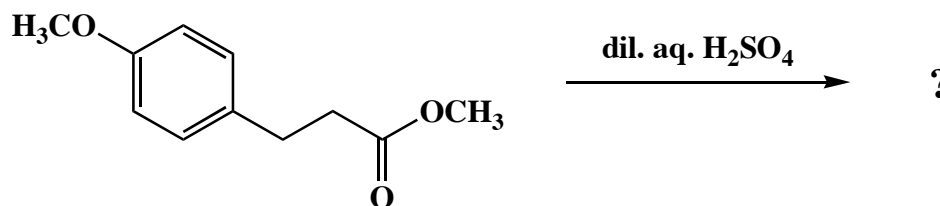
C. Bender's work showed that most reactions of carboxylic acid derivatives occur via

1. an  $S_N1$  mechanism
2. an  $S_N2$  mechanism
3. a nucleophilic addition/elimination mechanism

D. The reaction of octanenitrile with diisobutylaluminum hydride followed by dilute aqueous acetic acid gives

1. a ketone
2. an aldehyde
3. a carboxylic acid

2. Draw the major organic product that is formed from the following reaction. The  $^1\text{H}$  NMR spectrum of this product is shown below. The labels next to each of the resonances signify the integrals and multiplicities observed in the spectrum (s = singlet, d = doublet, t = triplet, br s = broad singlet). Use this spectroscopic evidence to determine the identity of the compound. Make clear assignments of all resonances to explain your reasoning. Finally, draw a detailed mechanism to show why the broad resonance at 11.0 ppm is  $\text{D}_2\text{O}$ -exchangeable.



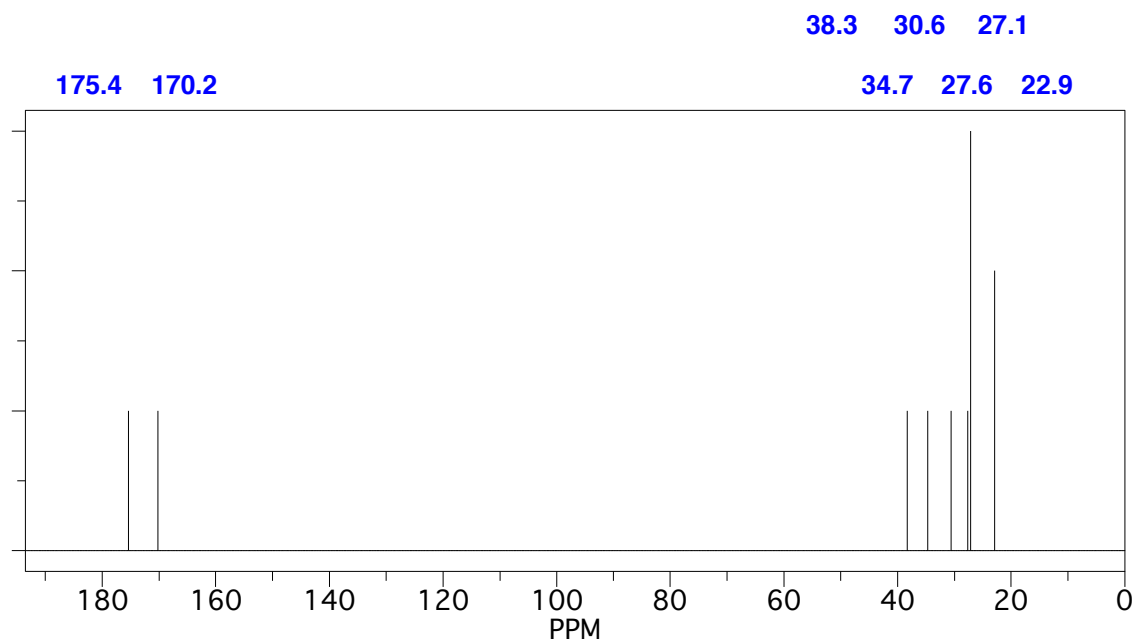
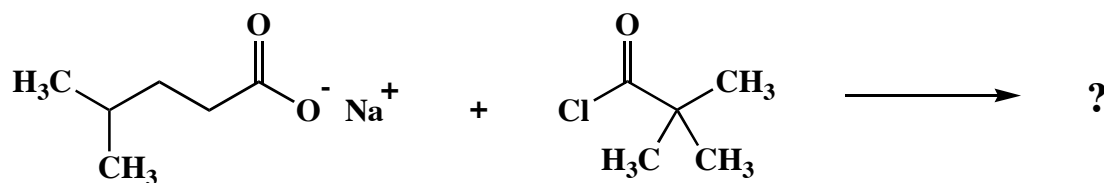
2. (continued)



**$^1\text{H}$  NMR assignments:**

<b>chemical shift (ppm)</b>	<b>assignment</b>	<b>explanation of multiplicity</b>
11.0		
7.01		
6.72		
3.73		
2.82		
2.56		

3. Draw the major organic product that is formed from the following reaction. The broadband proton-decoupled  $^{13}\text{C}$  NMR spectrum of this product is shown below. DEPT 90 and DEPT 135 data are included in the table on the following page. Use this spectroscopic evidence to determine the identity of the compound. Make clear assignments of all resonances to explain your reasoning. Finally, draw a detailed mechanism to show how the product is formed.



3. (continued)



**$^{13}\text{C}$  NMR assignments:**

<b>chemical shift (ppm)</b>	<b>assignment</b>	<b>DEPT 90</b>	<b>DEPT 135</b>	<b>DEPT explanation</b>
175.4		absent	absent	
170.2		absent	absent	
38.3		absent	absent	
34.7		absent	down	
30.6		absent	down	
27.6		present	up	
27.1		absent	up	
22.9		absent	up	