# Practice Tests, Organic Chemistry 2 Table of Contents

Online Organic Chemistry 2, Chem 360, Dr. Craig P. Jasperse, Minnesota State University Moorhead For full class website, see

https://collaborate.mnstate.edu/public/blogs/jasperse/online-organic-chemistry-courses/online-organic-chemistry-ii-360-fall-spring/

| <u>Test</u>      | <u>Page</u> |
|------------------|-------------|
| Test 1 Version 1 | 3           |
| Test 1 Version 2 | 9           |
| Test 1 Version 3 | 15          |
| Test 1 Version 4 | 21          |
|                  |             |
| Test 2 Version 1 | 27          |
| Test 2 Version 2 | 35          |
| Test 2 Version 3 | 43          |
| Test 2 Version 4 | 51          |
|                  |             |
| Test 3 Version 1 | 61          |
| Test 3 Version 2 | 67          |
| Test 3 Version 3 | 75          |
|                  |             |
| Test 4 Version 1 | 81          |
| Test 4 Version 2 | 87          |
| Test 4 Version 3 | 93          |
|                  |             |
| Final Exam       | 101         |

JASPERSE CHEM 360 TEST 1 Alcohols and Retrosynthesis

VERSION 1

1. Give the major product for the following reactions. (3 points each)

$$\begin{array}{c}
O \\
\hline
 & 1. \\
\hline
 & MgBr \\
\hline
 & 2. \\
\hline
 & H_3O^+
\end{array}$$

Ph 
$$\sim$$
 OH  $\stackrel{\text{H}_2\text{CrO}_4}{\longrightarrow}$ 

$$\begin{array}{c}
0 \\
\hline
1. \text{ LiAlH}_4 \\
\hline
2. \text{ H}_3\text{O}^+
\end{array}$$

2. Give Names or structures for the following: (9 points)

para-ethylphenol

3. For each of the following pairs, <u>circle</u> the one that is <u>higher boiling</u> and put a <u>square</u> around the one with the <u>higher water solubility</u>. (4 points)

- 4. Which of the following statements is **true**? (4 points)
- a. When an ether solution of **A** and **B** in a separatory funnel is treated with neutral water, only **B** remains in the ether layer.
- b. When an ether solution of **A** and **B** in a separatory funnel is treated with neutral water, neither **A** nor **B** remains in the ether layer.
- c. When an ether solution of **A** and **B** in a separatory funnel is treated with basic water (NaOH/H<sub>2</sub>O), both **A** and **B** remain in the ether layer.
- d. When an ether solution of **A** and **B** in a separatory funnel is treated with basic water (NaOH/H<sub>2</sub>O), only **B** remains in the ether layer.

- 5. For the following transformation, which of the following statements is true? (4 points)
- a. **D** is the only acceptable solvent
- b. C is the only acceptable solvent
- c. C and D are both acceptable solvents
- d. B, C, and D are all acceptable solvents
- e. A and B are the only acceptable solvents

Br 1. Mg, solvent OH

2. 
$$H_2C=O$$
3.  $H_3O^+$ 

Solvent Options

 $H_2O$   $CH_3OH$ 
 $A$   $B$   $C$   $D$ 

Formula C<sub>5</sub>H<sub>10</sub>O

Hydrogenation Test  $H_2/Pt$  No reaction Chromic Acid Test  $H_2CrO_4$  Turns Green

Lucas Test HCl/ZnCl<sub>2</sub> Reacts within 5 minutes

7. Provide the mechanisms for the following reactons (3, 5, and 5 points)

$$\stackrel{\text{O}}{\longleftarrow} \frac{1. \text{ LiAlH}_4}{2. \text{ H}_3\text{O}^+} \stackrel{\text{OH}}{\longleftarrow}$$

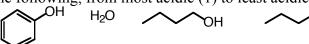
$$\begin{array}{c} O \\ \hline \\ Cl \end{array} \xrightarrow[2.\ H_3O^+]{} \begin{array}{c} OH \\ \hline \\ Me \end{array} ("Me"=methyl=CH_3)$$

$$\underbrace{\qquad \qquad}_{\text{Me}}^{\text{OH}} \xrightarrow{\text{H-Br}} 
\underbrace{\qquad \qquad}_{\text{Me}}^{\text{Br}}$$

8. Provide the reagents necessary to accomplish the following transformations (4 points each)

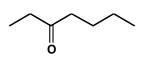
$$Ph$$
  $Br$   $Ph$   $OH$   $Ph$   $OH$   $(2-3 steps)$ 

9. Rank the acidity of the following, from most acidic (1) to least acidic (4). (4 points)



10. Design syntheses of the following. (6 points each). Allowed starting materials (same as practice) include:

cyclopentanol ethylene oxide formaldehyde iodomethane any esters any acyclic alcohol or alkene wth ≤4 carbons any "inorganic" agents (things that won't contribute carbons to your skeleton)



# JASPERSE CHEM 360 TEST 1 Alcohols and Retrosynthesis

#### **VERSION 2**

1. Give Names or structures for the following: (9 points) ortho-chlorophenol

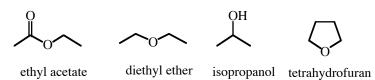
2. For each of the following pairs, <u>circle</u> the one that is <u>higher boiling</u> and put a <u>square</u> around the one with the higher water solubility. (4 points)

3. Of the listed four chemicals, circle those which <u>would ionize methanol</u> (convert it to sodium or magnesium methoxide)? (4 points)

Na NaNH<sub>2</sub> NaOH CH<sub>3</sub>MgBr

4. If an ether solution of the following three compounds was washed with NaOH/H<sub>2</sub>O, which (if any) of the compounds <u>would remain in the ether layer?</u> Circle any that would. (3 points)

5. Of the following common solvents, circle those that are <u>unsuitable</u> as solvents for the preparation and reactions of Grignard reagents (assuming you want the Grignard reagent to react with something else). (3 points)



6. Give the major product of the following reactions. (3 points each)

Ph
$$MgBr$$
  $\frac{1. OCH_3}{2. H_3O^+}$ 

$$\begin{array}{c} \begin{array}{c} \begin{array}{c} \\ \\ \end{array} \end{array} \begin{array}{c} \begin{array}{c} 1. \text{ LiAlH}_4 \\ \\ \hline \\ 2. \text{ H}_3\text{O}^+ \end{array} \end{array}$$

$$\sim$$
OH  $\frac{\text{H}_2\text{CrO}_4}{}$ 

7. Draw mechanisms for the following reactions. (3, 5, and 5 points)

Ph OMe 
$$\frac{1. \text{ LiAlH}_4}{2. \text{ H}_3\text{O}^+} \text{ Ph OH}$$

$$\bigvee^{OH} \xrightarrow{HBr} \bigvee^{Br}$$

8. Suggest a possible structure for an unknown  $\bf A$  whose formula is  $C_6H_{12}O$ , and gives the following chemical test results: (Double check that your answer is consistent with all the data) 5 pt

Formula:  $C_6H_{12}O$ 

Hydrogenation Test H<sub>2</sub>/Pt No reaction

 $\begin{array}{lll} \text{Chromic Acid Test} & \text{H}_2\text{CrO}_4 & \text{Turns green} \\ \text{Lucas Test} & \text{HCl/ZnCl}_2 & \text{No reaction} \end{array}$ 

9. Provide reagents for the following transformations. ("workup" means  $H_3O^+$  or  $H_2O$  steps) (First two are 3 points each; last four are 5 points each)

Note: In this test, I had allowed alcohols

of up to 5 carbons, not limited to only 4.

10. Design syntheses for the following. Allowed starting materials (same as practice) include: bromobenzene 6 points each

cyclopentanol

any acyclic alcohol or alkene with ≤5 carbons

any esters

ethylene oxide

formaldehyde (CH<sub>2</sub>O)

iodomethane

any "inorganic" agents (things that won't contribute carbons to your skeleton)

### JASPERSE CHEM 360 TEST 1 Reactions involving Alcohols

**VERSION 3** 

1. 2-Methylpentan-3-ol is classified as: (3 points)

- a. a primary alcohol b. a secondary alcohol
- c. a tertiary alcohol d. none of the above
- 2. Provide acceptable names for the following: (10 points total)



racemic

3. Circle the molecule with the highest boiling point. Put a square around the molecule with the highest water solubility. (4 points)



4. Rank the acidity of the following molecules, from 1 (strongest) to 4 (weakest). Explain <u>very briefly</u> why **A** and **B** have very different acidities.

 $H_2O$ 

 $CH_4$ 

A

В

5. Draw the major products for the following reactions. (Assume excess quantities of reagents.) (3 points each, 21 points total)

$$OCH_3 \xrightarrow{1. CH_3CH_2MgBi}$$

$$2. H_3O^+$$

$$\begin{array}{c} & \xrightarrow{\text{H}_2\text{CrO}_4} \end{array}$$

6. Which of the following would be suitable to use when forming a Grignard reagent? (3 points)

$$Br$$
  $Br$   $NH_2$   $Br$ 

7. Provide the reagents necessary to accomplish the following transformations (5 each, 20 total)

8. Draw a possible structure for an <u>achiral</u> molecule  $\bf A$  with formula  $C_5H_{12}O$ , given that when  $H_2CrO_4$  is added to  $\bf A$  the solution turns green, and that the Lucas test with  $\bf A$  takes about 3-4 minutes. (5 points)

9. Draw the mechanisms for the following transformations. <u>Identify the slow step in each mechanism</u>. (6 points each)

$$\begin{array}{cccc}
O & \frac{1. \ 2 \ PhMgBr}{2. \ H_3O^+} & OH \\
\end{array}$$

10. Design syntheses of the following, starting from alcohols of ≤4 carbons. (7 points each)

JASPERSE CHEM 360 TEST 1 Reactions Involving Alcohols

**VERSION 4** 

- 1. Provide Names or Structures for the Following. (10 points total)
- a. (2R,5R)-(Z)-5-methylhept-3-en-2-ol

2. Rank the acidity of the following molecules, 1 being most and 4 being least acidic. (3 points)

$$CH_{3}NH_{2} \hspace{1cm} OH \hspace{1cm} (CH_{3})_{2}CHOH \hspace{1cm} H_{2}O$$

3. Complete the following acid-base reactions, and indicate whether the equilibrium favors the reactants or the products. (3 points each)

4. Draw the products of the following reactions. (3 points each)

a. 
$$\overbrace{ \begin{array}{c} NaBH_4, \\ H_2O \end{array} }$$

d. Ome 
$$\frac{1. \text{ LiAlH}_4}{2. \text{ H}_3\text{O}^+}$$

e. 
$$\frac{1. \text{ MeMgBr}}{2. \text{ H}_2\text{O}^+}$$

f. 
$$\stackrel{\text{H. OH}}{\longrightarrow}$$
  $\frac{1. \text{ Na}}{2. \text{ CH}_3\text{CH}_2\text{I}}$ 

5. Draw the products for the following multistep syntheses. (5 points each)

b. 1. NaBH<sub>4</sub>, H<sub>2</sub>O
2. PBr<sub>3</sub>
3. Mg
4. Me<sub>2</sub>C=O
5. H<sub>3</sub>O<sup>+</sup>

6. Draw the mechanism for the following reaction. (6 points)

$$\begin{array}{ccc}
O & & 1. \text{ PhMgBr} \\
O\text{CH}_{3} & & & & Ph
\end{array}$$

7. Draw the mechanism for the following reaction. Note: This is a slight twist on familiar stuff. The overall transformation appears unfamiliar, but the individual steps are actually familiar. (6 pts)

8. Suggest a structure for a compound "A" whose formula is  $C_5H_{12}O$ , that reacts instantly with the Lucas reagent (ZnCl<sub>2</sub>/HCl), but does not cause an orange to green color change upon mixing with chromic acid. (4 points)

9. Provide reagents for the following transformations. For this problem, you may use absolutely any reactant you please, including carbonyl compounds or organometallics (so long as it does not include more than one functional group). I have indicated the number of steps I envision, to give you an idea if your route is longer or shorter than necessary. (You may design alternate routes longer, or perhaps even shorter, than the ones I have in mind.) (6 points each)

a. 
$$\bigcirc$$
 OH  $\bigcirc$  (5 steps, counting  $H_3O^+$ )

c. 
$$\longrightarrow$$
 OH  $\longrightarrow$  (4 steps, counting  $H_3O^+$ )

10. Provide a synthesis for the following molecules. Permissible starting materials include cyclopentanol, acyclic alcohols or alkenes of  $\leq 5$  carbons, formaldehyde, ethylene oxide, esters, and any other support reagents you like. (7 points each) (In none of these examples should it take more than 5 steps to get from any starting material to the products.)

1. Predict the <sup>1</sup>H NMR spectrum. Include the source (CH<sub>3</sub>-1, etc); approximate chemical shifts (1's, 2's, etc.); integration (1H, 2H, etc.); and splitting (either list the number of lines, or else use letters: "s" for singlet; "d" for doublet etc.). If signals are symmetry equivalent, do <u>not</u> list them twice.

|    | Source | Chem Shift | <u>Integration</u> | Splitting |
|----|--------|------------|--------------------|-----------|
|    |        |            |                    |           |
| O. |        |            |                    |           |
|    |        |            |                    |           |
|    |        |            |                    |           |
|    |        |            |                    |           |
|    |        |            |                    |           |
|    |        |            |                    |           |
|    |        |            |                    |           |
|    |        |            |                    |           |

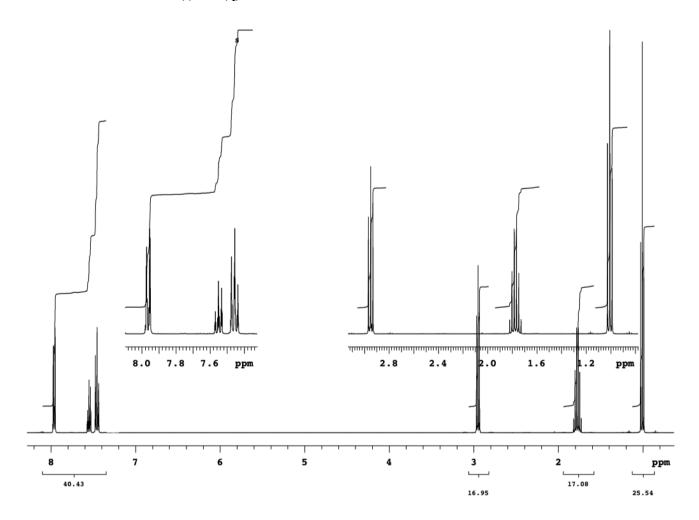
2. Predict the <sup>13</sup>C NMR spectrum. Include the approximate chemical shifts (220-160, 160-100, 100-50, or 50-0) and the splitting if a coupled carbon NMR was taken (can either use letters, q, t, d, s, or else number of lines).

| number of fines). |            |                        |           |
|-------------------|------------|------------------------|-----------|
|                   | Source     | Approximate Chem Shift | Splitting |
| O OH              | C1         |                        |           |
|                   | C2         |                        |           |
| 2 4 6             | C3         |                        |           |
| 3 5               | <b>C</b> 4 |                        |           |
|                   | C5         |                        |           |
|                   | C6         |                        |           |
|                   | C7         |                        |           |
|                   |            |                        |           |

- 3. Match the following structures with the listed feature IR signals. (Write the letter of the structure by the IR signal):
  - 1) 3300-3400
- 2) 3300-2500, 1680
- 3) 2200
- 4) 1710

For the remainder of the test, solve the structures for the following. If you get a structure perfect, you will get full credit. If you do not get a structure perfect, you may still get some partial credit. Thus, it is in your interest to show some of you work, make a structure, or tell me what you know for sure.

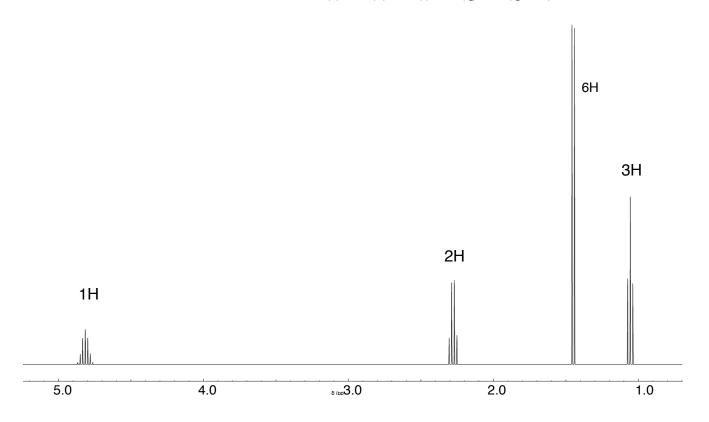
4.  $C_{10}H_{12}O$  IR: 1670 IR: 1670 IR: 1670 IR: 170 (s, short), 150 (s, short), 130 (d, tall), 124 (d, tall), 120 (d), 33 (t), 26 (t), 20 (q)



5. C<sub>6</sub>H<sub>12</sub>O<sub>2</sub>

IR: 1745

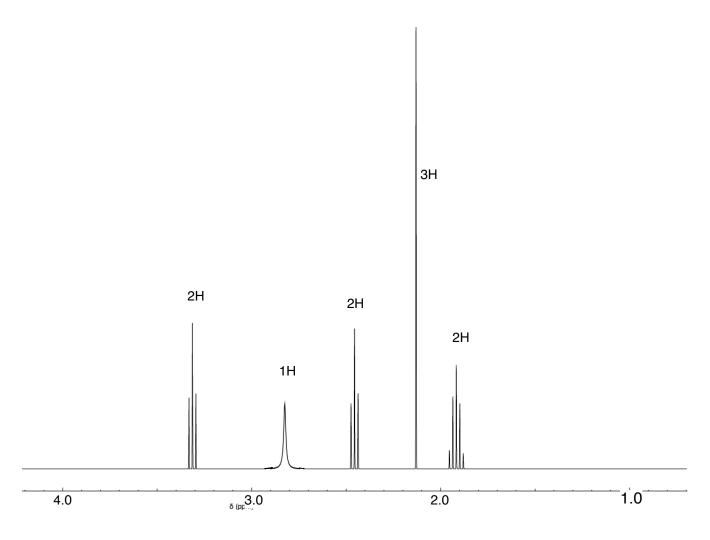
<sup>13</sup>C: 180 (s), 70 (d), 36 (t), 30 (q), 20 (q, tall)



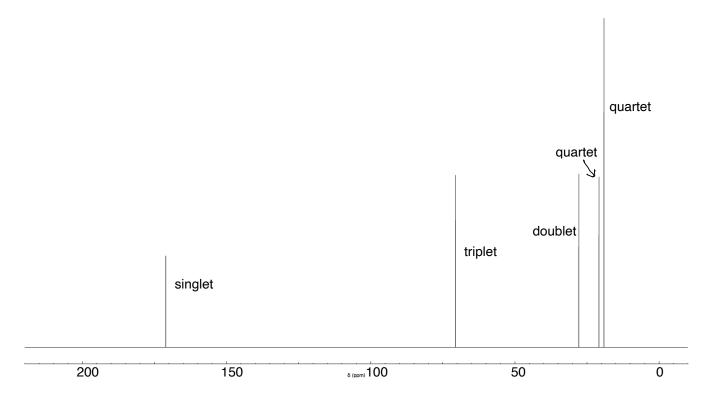
6. C<sub>5</sub>H<sub>10</sub>O<sub>2</sub>

IR: 3300-3200, 1710

<sup>13</sup>C: 210 (s), 65 (t), 38 (t), 35 (t), 28 (q)

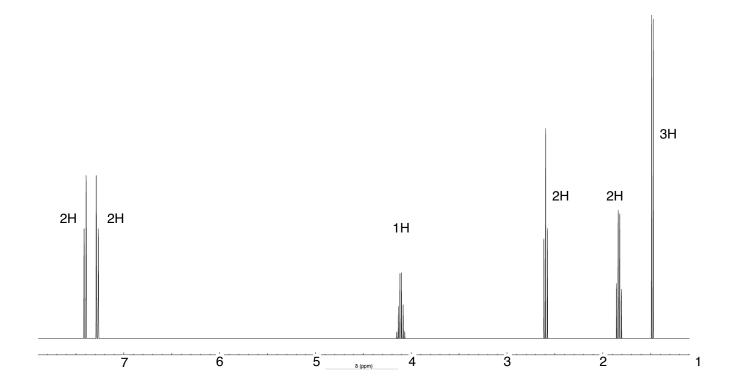


- 7.  $C_6H_{12}O_2$
- IR: 1745
- The spectrum displayed is a "decoupled" 13-C NMR spectrum. (No splitting)
- But beside each coupled peak is a label that tells whether the carbon would be a singlet, doublet, triplet, or quartet \*\*if\*\* a "coupled" 13-C NMR had been obtained.
- (Note: There are two plausible solutions to this problem)



8.  $C_{10}H_{12}Cl_2$ 

<sup>13</sup>C: 150 (s), 144 (s), 133 (d), 126 (d), 58 (d), 37 (t), 32 (t), 22 (q)



IR: 3300-3200

13C NMR: 78 (d), 40 (d), 36 (t), 25 (q), 20 (q, extra tall)

6H, d, 1.0 3H, t, 1.2

2H, pentet, 1.4

1H, octet, 1.8

1H, broad s, 3.0

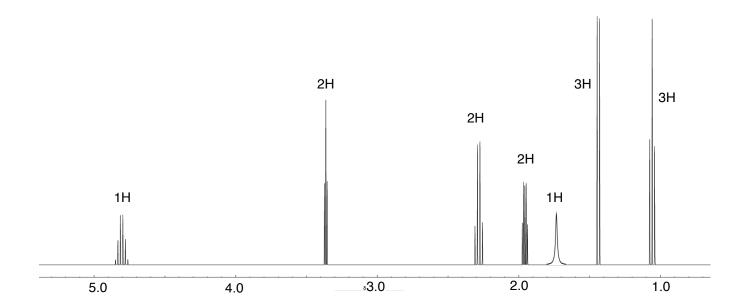
1H, q, 3.8

10. C<sub>7</sub>H<sub>14</sub>O<sub>3</sub>

IR: 3300-3200, 1745

13C-NMR: 180 (s), 75 (d), 65 (t), 38 (t), 30 (t), 25 (q), 20 (q)

Either of 2 answers will be accepted for this question.



I have not, accidentally or intentionally, seen copies or parts of the test in advance, including online. In the event that I did, I will report this to the instructor as soon as possible.

Chem 360-Jasperse Test #2

NMR, IR

Version 2

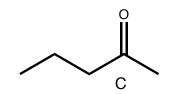
1. Predict the <sup>1</sup>H NMR spectrum. Include the source (CH<sub>3</sub>-1, etc); approximate chemical shifts (1's, 2's, etc.); integration (1H, 2H, etc.); and splitting (either list the number of lines, or else use letters: "s" for singlet; "d" for doublet etc.). If signals are symmetry equivalent, do <u>not</u> list them twice.

| Source | Chem Shift | Integration | Splitting |
|--------|------------|-------------|-----------|
| Source | Chem Shine | integration | Spitting  |

2. Predict the <sup>13</sup>C NMR spectrum. Include the approximate chemical shifts (220-160, 160-100, 100-50, or 50-0) and the splitting if a coupled carbon NMR was taken (can either use letters, q, t, d, s, or else number of lines).

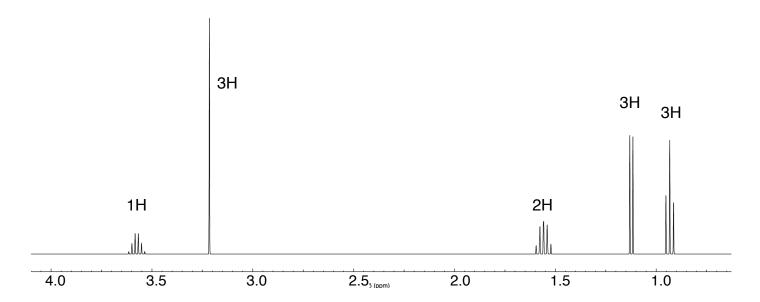
| _                          | Source | Approximate Chem Shift | Splitting |
|----------------------------|--------|------------------------|-----------|
| 0<br>                      | C1     |                        |           |
|                            | C2     |                        |           |
| 0 1 / 2                    | C3     |                        |           |
| \ <u>4</u> // <sub>3</sub> | C4     |                        |           |
|                            | C5     |                        |           |
| 5                          |        |                        |           |
| 1                          |        |                        |           |

3. Match the following structures with the listed feature IR signals. (Write the letter of the structure by the IR signal):



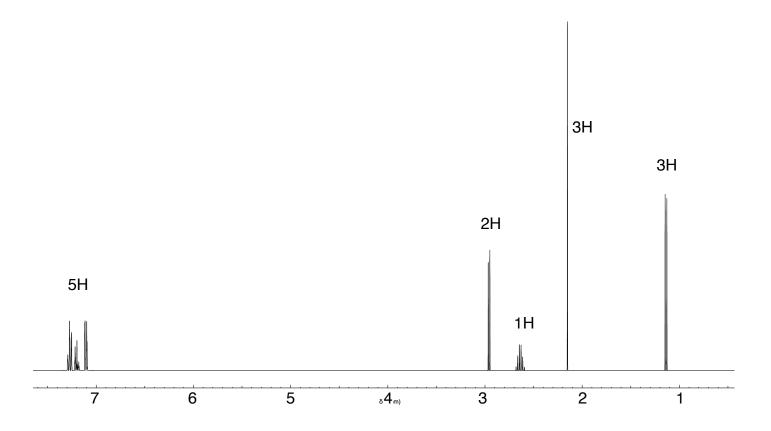
For the remainder of the test, solve the structures for the following. If you get a structure perfect, you will get full credit. If you do not get a structure perfect, you may still get some partial credit. Thus, it is in your interest to show some of you work, make a structure, or tell me what you know for sure.

## 4. C<sub>5</sub>H<sub>12</sub>O IR: Nothing interesting



5.  $C_{11}H_{14}O$  IR: 1710 <sup>13</sup>C: 211 (s), 139 (s), 134 (d), 127 (d), 122 (d), 42 (d), 35 (t), 20 (q), 15 (q)

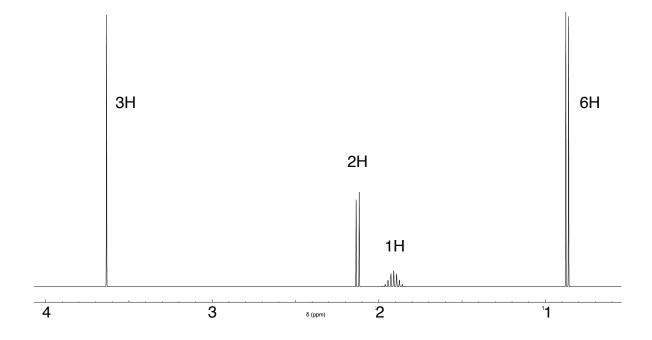
• (Note: There are two plausible solutions to this problem)



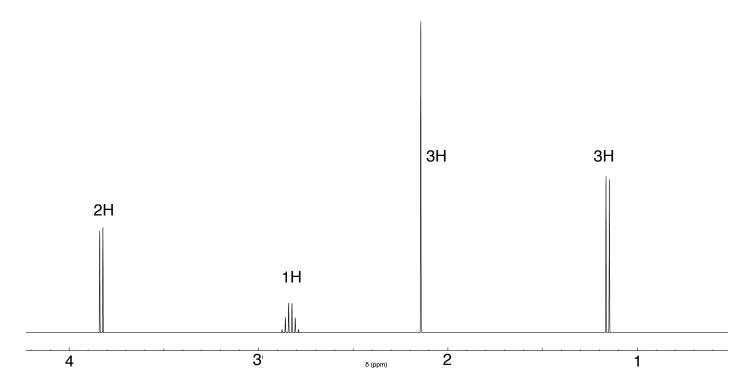
6. C<sub>6</sub>H<sub>12</sub>O<sub>2</sub>

IR: 1745

<sup>13</sup>C: 170 (s), 65 (q), 42 (t), 37 (d), 18 (q)



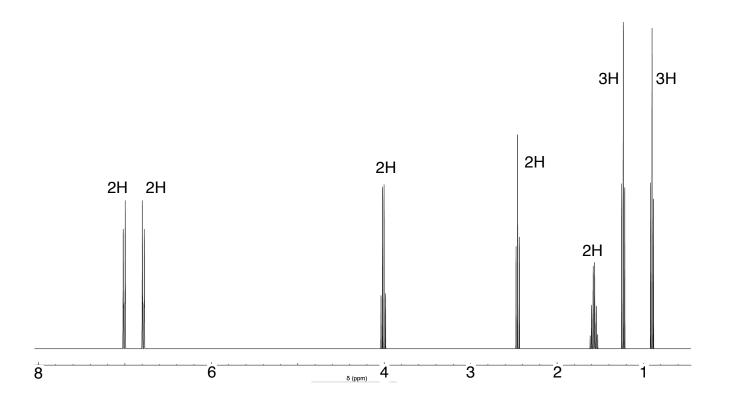
7. C<sub>5</sub>H<sub>9</sub>OCl IR: 1710



 $C_{11}H_{16}O$ 8.

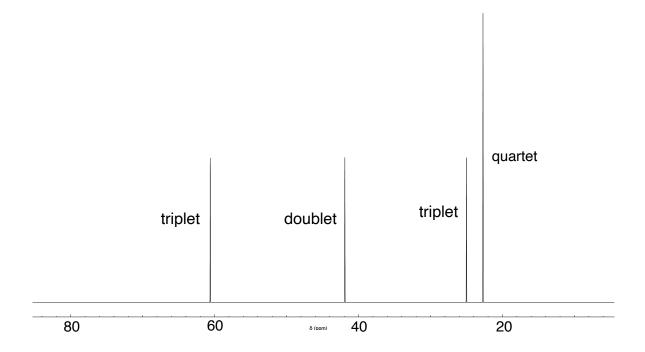
IR: Nothing interesting

13C: 148 (s), 140 (s), 130 (d), 125 (d), 64 (t), 38 (t), 25 (t), 15 (q), 14 (q)



## 9. C<sub>5</sub>H<sub>12</sub>O

- The spectrum displayed is a "decoupled" 13-C NMR spectrum. (No splitting)
- But beside each coupled peak is a label that tells whether the carbon would be a singlet, doublet, triplet, or quartet \*\*if\*\* a "coupled" 13-C NMR had been obtained.



10. C<sub>6</sub>H<sub>12</sub>O<sub>2</sub> IR: 1745

0.92, 3H, triplet

1.12, 3H, doublet

1.54, 2H, pentet

2.38, 1H, sextet

3.89, 3H, s

• I have not, accidentally or intentionally, seen copies or parts of the test in advance, including online. In the event that I did, I will report this to the instructor as soon as possible.

1. Predict the <sup>1</sup>H NMR spectrum. Include the source (CH<sub>3</sub>-1, etc); approximate chemical shifts (1's, 2's, etc.); integration (1H, 2H, etc.); and splitting (either list the number of lines, or else use letters: "s" for singlet; "d" for doublet etc.). If signals are symmetry equivalent, do <u>not</u> list them twice.

| Source | Chem Shift | Integration | Splitting |
|--------|------------|-------------|-----------|
|        |            |             |           |
|        |            |             |           |
|        |            |             |           |
|        |            |             |           |
|        |            |             |           |

2. Predict the <sup>13</sup>C NMR spectrum. Include the approximate chemical shifts (220-160, 160-100, 100-50, or 50-0) and the splitting if a coupled carbon NMR was taken (can either use letters, q, t, d, s, or else number of lines).

| indifficer of fines). | Source | Approximate Chem Shift | Splitting |
|-----------------------|--------|------------------------|-----------|
| 0                     | C1     |                        |           |
| l II                  | C2     |                        |           |
| $\frac{1}{2}$         | C3     |                        |           |
| 1 6                   | C4     |                        |           |
|                       | C5     |                        |           |
|                       | C6     |                        |           |
|                       | C7     |                        |           |

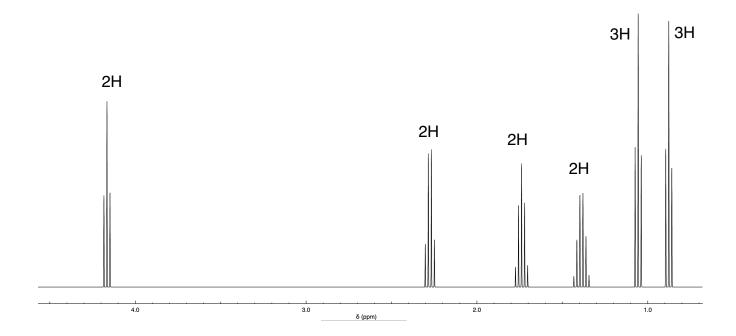
3. Match the following structures with the listed feature IR signals. (Write the letter of the structure by the IR signal):

For the remainder of the test, solve the structures for the following. If you get a structure perfect, you will get full credit. If you do not get a structure perfect, you may still get some partial credit. Thus, it is in your interest to show some of you work, make a structure, or tell me what you know for sure.

4.  $C_7H_{14}O_2$  I

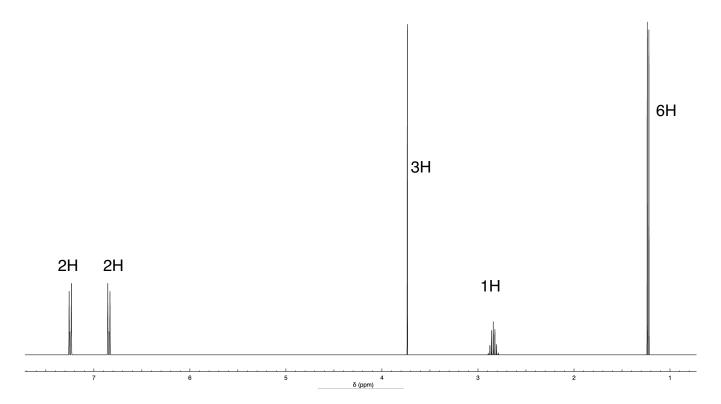
IR: 1745

<sup>13</sup>C NMR: 175 (s, short), 65 (t), 32 (t), 28 (t), 19 (t) 14 (q), 9 (q)



5.  $C_{10}H_{14}O$  IR: nothing interesting

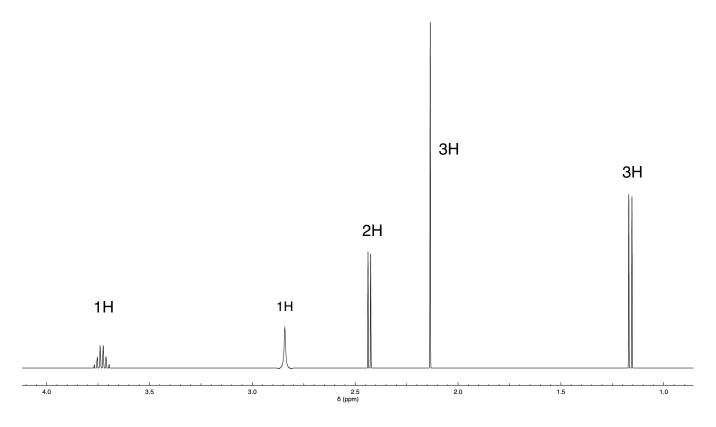
<sup>13</sup>C: 158 (s), 141 (s), 128 (d), 114 (d), 65 (q), 33 (d), 24 (q, tall)



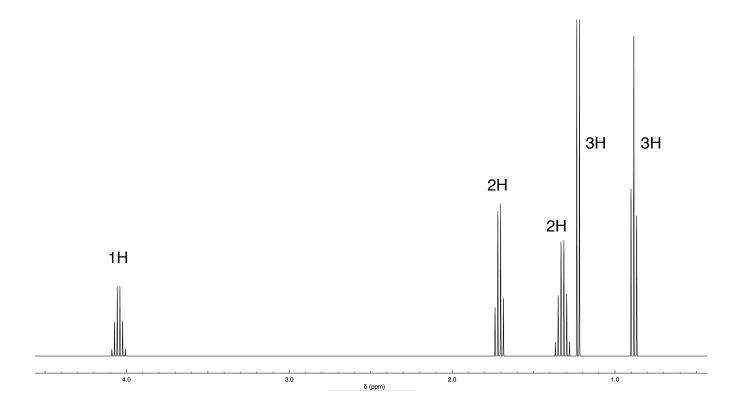
6. C<sub>5</sub>H<sub>10</sub>O<sub>2</sub>

IR: 3300-3200, 1710

<sup>13</sup>C: 210 (s), 65 (d), 40 (t), 30 (q), 23 (q)



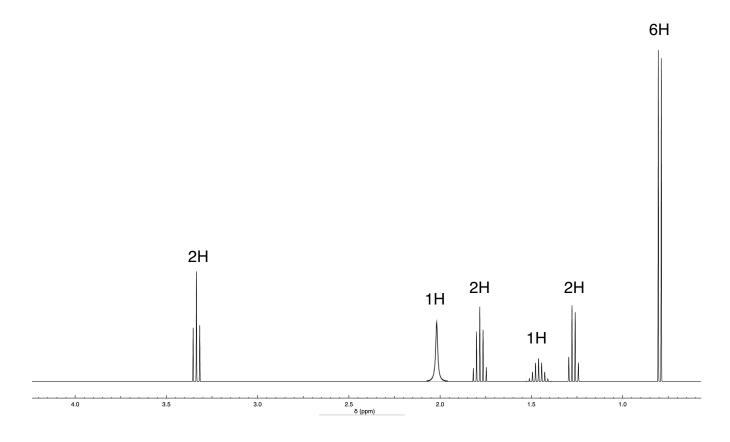
7. C<sub>5</sub>H<sub>11</sub>Cl



8.

C<sub>6</sub>H<sub>14</sub>O IR: 3300-3200

<sup>13</sup>C: 63 (t), 34 (t), 30 (t), 27 (d), 22 (q, tall)



9. C<sub>6</sub>H<sub>12</sub>O<sub>2</sub> IR: 1745

13C NMR: 172 (s), 61 (t), 36 (t), 19 (t), 14 (q), 13 (q)

0.92, 3H, triplet

1.15, 3H, triplet

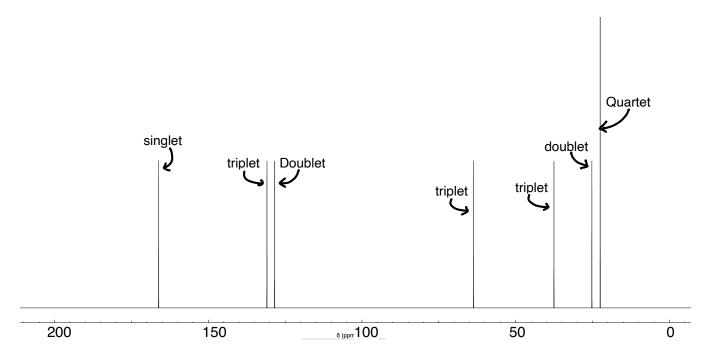
1.62, 2H, sextet

2.22, 2H, triplet

4.10, 2H, quartet

## 10. $C_8H_{14}O_2$

- The spectrum displayed is a "decoupled" 13-C NMR spectrum. (No splitting)
- But beside each coupled peak is a label that tells whether the carbon would be a singlet, doublet, triplet, or quartet \*\*if\*\* a "coupled" 13-C NMR had been obtained.
- Four different answers are all plausible for this.



• I have not, accidentally or intentionally, seen copies or parts of the test in advance, including online. In the event that I did, I will report this to the instructor as soon as possible.

1. Predict the <sup>1</sup>H NMR spectrum. Include the source (CH<sub>3</sub>-1, etc); approximate chemical shifts (1's, 2's, etc.); integration (1H, 2H, etc.); and splitting (either list the number of lines, or else use letters: "s" for singlet; "d" for doublet etc.). If signals are symmetry equivalent, do not list them twice.

|       | Source | Chem Shift | Integration | <u>Splitting</u> |
|-------|--------|------------|-------------|------------------|
| 0     |        |            |             |                  |
| Ĭ     |        |            |             |                  |
|       |        |            |             |                  |
| 0 2 4 |        |            |             |                  |
| 1 3 5 |        |            |             |                  |
|       |        |            |             |                  |
|       |        |            |             |                  |

2. Predict the <sup>13</sup>C NMR spectrum. Include the approximate chemical shifts (220-160, 160-100, 100-50, or 50-0) and the splitting if a coupled carbon NMR was taken (can either use letters, q, t, d, s, or else number of lines).

| number of fines). |        |                        | ,         |
|-------------------|--------|------------------------|-----------|
|                   | Source | Approximate Chem Shift | Splitting |
| 0                 | C1     |                        |           |
|                   | C2     |                        |           |
| 2 0 3 4 5 6       | C3     |                        |           |
| 1                 | C4     |                        |           |
|                   | C5     |                        |           |
|                   | C6     |                        |           |
|                   |        |                        |           |

3. Match the following structures A, B, and C with the listed feature IR signals.

| 1) 3300-3400 | 0 | o<br>            | , OH |
|--------------|---|------------------|------|
| 2) 1745      |   | OCH <sub>3</sub> |      |
| 3) 1710      | A | В                | C    |

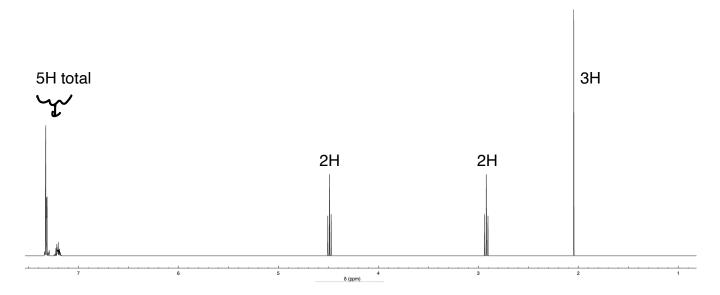
4. Match the dimethyl benzene isomer for which the <sup>13</sup>C NMR spectrum has:.

For the remainder of the test, solve the structures for the following. If you get a structure perfect, you will get full credit. If you do not get a structure perfect, you may still get some partial credit. Thus, it is in your interest to show some of you work, make a structure, or tell me what you know for sure.

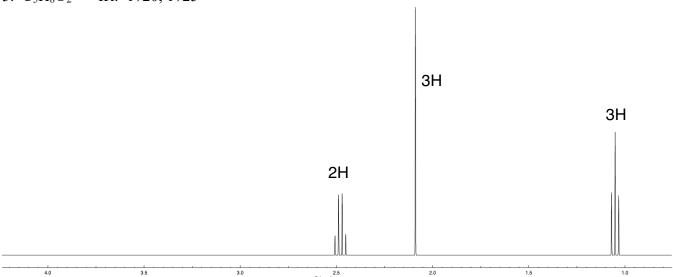
5.  $C_{10}H_{12}O_2$ 

IR: 1745

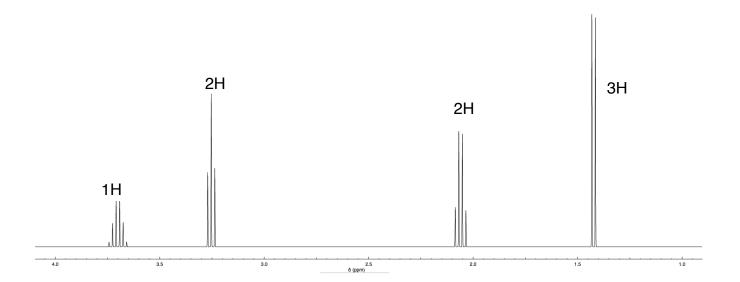
<sup>13</sup>C NMR: 185 (s), 155 (s), 135 (d), 130 (d), 128 (d), 65 (t), 28 (t), 19 (q)







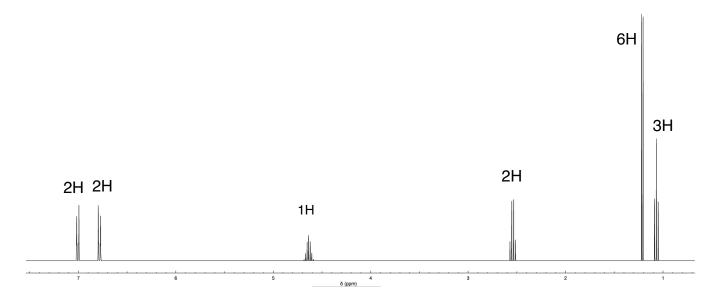
IR: Nothing interesting

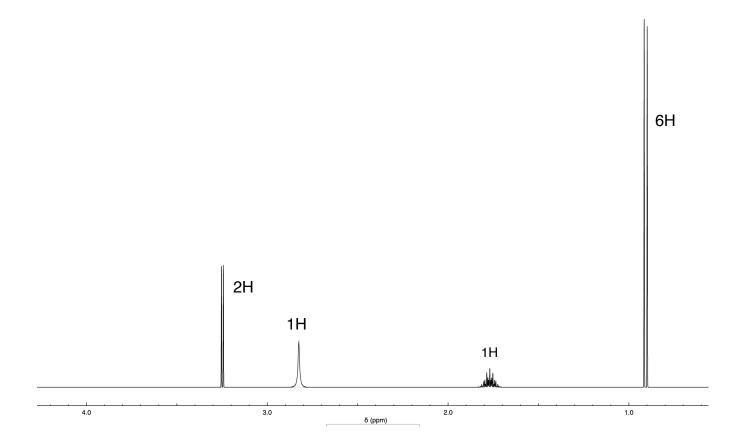


7.  $C_{11}H_{16}O$ 

IR: nothing interesting

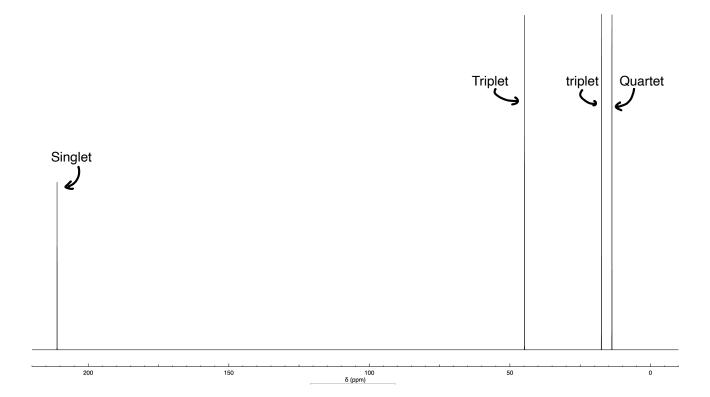
13C: 158 (s), 141 (s), 128 (d), 114 (d), 65 (d), 29 (t), 22 (q, tall), 15 (q)





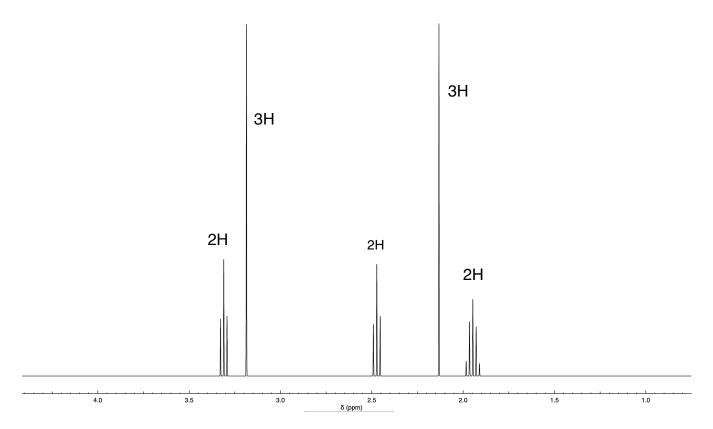
IR: 1710

- The spectrum displayed is a "decoupled" 13-C NMR spectrum. (No splitting)
- But beside each coupled peak is a label that tells whether the carbon would be a singlet, doublet, triplet, or quartet \*\*if\*\* a "coupled" 13-C NMR had been obtained.



10.  $C_6H_{12}O_2$ 

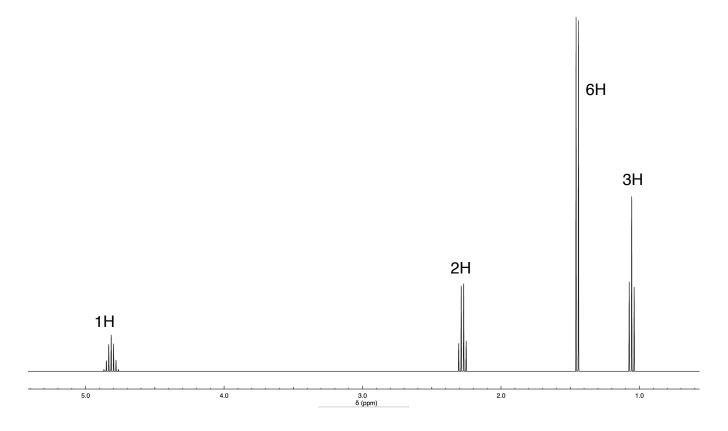
IR: 1710 13C-NMR: 210 (s), 75 (t), 65 (q), 40 (t), 30 (t), 20 (q), 20 (q)



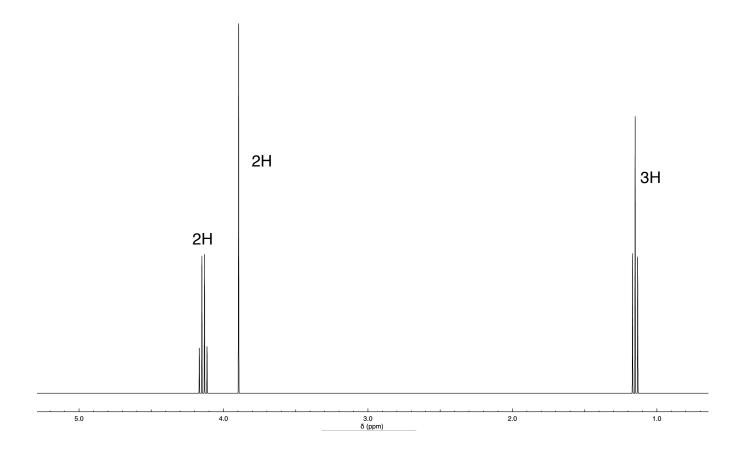
11.  $C_6H_{12}O_2$ 

IR: 1745

13C-NMR: 185 (s), 78 (d), 42 (t), 30 (q), 20 (q)



11. C<sub>4</sub>H<sub>7</sub>O<sub>2</sub>Br IR: 1745



• I have not, accidentally or intentionally, seen copies or parts of the test in advance, including online. In the event that I did, I will report this to the instructor as soon as possible.

JASPERSE CHEM 360 TEST 3

VERSION 1

Ch 18 Ketones and Aldehydes

Ch 22 Additions and Conensations of Enols and Enolate Ions

1. Provide the Name for the Following (6 points)

- 2. Of the following structures,
- a. Which will be "completely" (>98%) deprotonated by LDA (LiN-iPr<sub>2</sub>)? (2 points)
- b. Which will be "completely" (>98%) deprotonated by NaOH? (2 points)

3. An unknown **X** has formula  $C_4H_8O$ . It gives 1) an orange precipitate upon treatment with 2,4-dinitrophenylhydrazine (2,4-DNP) and it gives 2) a silver mirror upon treatment with Tollen's reagent  $[Ag(NH_3)_2^+OH^-]$ . 3) It does not react with  $Br_2$  in dichloromethane solvent. 4) Included in the H NMR (incomplete) is a 6H doublet at 1.2 ppm. What is **X**? (4 points)

4. Rank the rate of decarboxylation (loss of  $CO_2$ ) for the following molecules upon heating, with 1 being highest, 2 being next, and 3 being not at all. [Hint: Two out of the three will react, one will not, so you should be able to identify the unreactive isomer. To compare the reactivity of the two reactive isomers, the phenyl substituent impacts the relative stabilities in the key step of the mechanism.] (2 points)

5. Synthesis Reactions. Draw the feature product of the following reactions (need not show any byproducts). NOTE: In every case, the product should be a stable, isolable **product**; an "intermediate" structure will not receive full credit. (2 or 3 points each; 1st 7 worth 2 points; last 5 worth 3 points each)

$$\begin{array}{c} \textbf{O} \\ \hline \\ \textbf{Ph} \end{array} \begin{array}{c} Br_2, \text{ excess} \\ \hline \\ \text{NaOMe, MeOH} \end{array}$$

6. Provide Reagents for the Following Transformations: (4 points each)

7. Put in the starting materials from which the following structures would be produced. Depending on the product, the appropriate starting material may be either a single molecule, two of the same molecule, or two different molecules. For the last problem, you are required to start from two separate molecules. (2 points each)

Note: The Starting Materials are two Separate Molecules

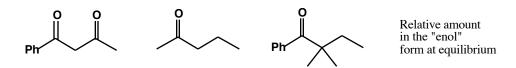
8. Design a synthesis for the following alkene, FROM ALCOHOLS WITH NO MORE THAN 5 CARBONS. (4 points)

9. Provide Mechanisms for the Following Transformations. [Note: Some of these do not represent "clean" reactions; the product shown might go on to further reactions, or the reaction might be reversible, or the product might not be isolable. But that shouldn't prevent you from drawing the mechanism for the transformation indicated!] (3 points each)

$$\begin{array}{c|c} \textbf{O} & & \textbf{OH} \\ \hline \\ \textbf{Ph} & & \textbf{Ph} & \textbf{OMe} \\ \end{array}$$

$$\begin{array}{c|c} \text{OH} & \xrightarrow{H_2O,\,H^+} & \text{O} \\ \\ \text{Ph} & & \\ \end{array}$$

## 10. Rank the following, with 1 being highest, or most. (2 points each)



JASPERSE **CHEM 360** TEST 3 **VERSION 2** 

Ch 18 Ketones and Aldehydes Ch 22 Additions and Conensations of Enols and Enolate Ions

1. Nomenclature. Provide the structure or the name for the following. If stereochemistry is a factor, do not neglect it. (6 pt)

3-isopropylbenzaldehyde

optically active

2. Rank the following, with 1 being highest, or most. (6 pt)

Equilibrium concentration of enol

Reactivity toward MeMgBr

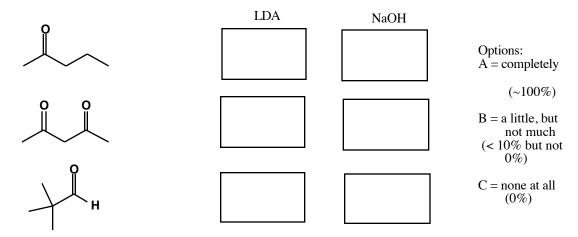
Acidity

3. Draw the products for the following reactions (3 pt each)

$$\mathbf{CH_3}\mathbf{-C}\mathbf{\equiv C}\mathbf{-H} \quad \frac{\mathbf{Hg^{2+}, H_2O}}{\mathbf{H_2SO_4}}$$

4. Draw the products for the following multistep reactions. (3 pt each)

5. For the following chemicals, describe the extent to which each would be deprotonated by LDA (LiN-iPr<sub>2</sub>) or by NaOH at equilibrium. Fill in all 6 boxes. Options are complete deprotonation (A), a little deprotonation (B), and no deprotonation (C). (6 pt)



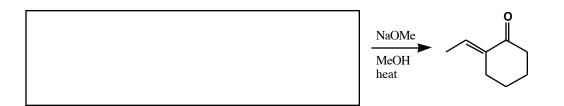
- 6. Suggest a plausible structure consistent with the following information. (5 pt)
- a. It reacts positively with 2,4-dinitrophenylhydrazine.
- b. It reacts positively with NaOH/I<sub>2</sub>, the iodoform test
- c. It does not react with Tollen's reagent [Ag(NH<sub>3</sub>)<sub>2</sub>+OH-].
- d. It does not react with Br<sub>2</sub> in dichloromethane solvent.
- e. Chemical formula is C7H12O
- f. It's <sup>13</sup>C spectrum shows 5 carbons (1 singlet, 1 doublet, 2 triplets, and 1 quartet)

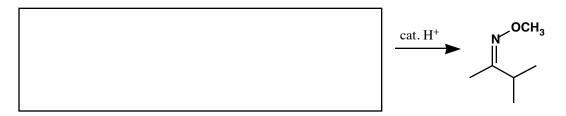
7. Which of the following would <u>not</u> undergo decarboxylation (loss of CO<sub>2</sub>) upon heating? (2 pt)

8. Put in the starting materials from which the following would be made. (3 each)

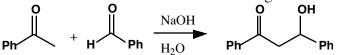








9. Draw the mechanisms for the following reactions. (4 pt each)



(Note: this one counts as 2 problems, 8 points total)

$$\begin{array}{c}
\bullet \\
\bullet \\
\bullet \\
\bullet
\end{array}$$

$$\begin{array}{c}
\bullet \\
\bullet \\
\bullet$$

$$\begin{array}{c}
\bullet \\
\bullet \\
\bullet
\end{array}$$

$$\begin{array}{c}
\bullet \\
\bullet \\
\bullet$$

$$\begin{array}{c}
\bullet \\
\bullet
\end{array}$$

$$\begin{array}{c}
\bullet \\
\bullet$$

$$\begin{array}{c}
\bullet \\
\bullet
\end{array}$$

$$\begin{array}{c}
\bullet \\
\bullet
\end{array}$$

$$\begin{array}{c}
\bullet \\
\bullet$$

$$\begin{array}{c}
\bullet \\
\bullet
\end{array}$$

$$\begin{array}{c}
\bullet \\
\bullet$$

$$\begin{array}{c}
\bullet \\
\bullet
\end{array}$$

$$\begin{array}{c}
\bullet \\
\bullet$$

$$\begin{array}{c}
\bullet \\
\bullet
\end{array}$$

$$\begin{array}{c}
\bullet \\
\bullet$$

$$\begin{array}{c}
\bullet \\
\bullet
\end{array}$$

$$\begin{array}{c}
\bullet \\
\bullet$$

$$\begin{array}{c}
\bullet \\
\bullet
\end{array}$$

$$\begin{array}{c}
\bullet \\
\bullet$$

$$\begin{array}{c}
\bullet \\
\bullet
\end{array}$$

$$\begin{array}{c}
\bullet \\
\bullet$$

$$\begin{array}{c}
\bullet \\
\bullet
\end{array}$$

$$\begin{array}{c}
\bullet \\
\bullet$$

$$\begin{array}{c}
\bullet \\
\bullet
\end{array}$$

$$\begin{array}{c}
\bullet \\
\bullet$$

$$\begin{array}{c}
\bullet \\
\bullet
\end{array}$$

$$\begin{array}{c}
\bullet \\
\bullet$$

$$\begin{array}{c}
\bullet \\
\bullet
\end{array}$$

$$\begin{array}{c}
\bullet \\
\bullet$$

$$\begin{array}{c}
\bullet \\
\bullet
\end{array}$$

$$\begin{array}{c}
\bullet \\
\bullet$$

$$\begin{array}{c}
\bullet \\
\bullet
\end{array}$$

$$\begin{array}{c}
\bullet \\
\bullet$$

$$\begin{array}{c}
\bullet \\
\bullet
\end{array}$$

$$\begin{array}{c}
\bullet \\
\bullet$$

$$\begin{array}{c}
\bullet \\
\bullet$$

$$\begin{array}{c}
\bullet \\
\bullet
\end{array}$$

$$\begin{array}{c}
\bullet \\
\bullet$$

$$\begin{array}{c}
\bullet \\
\bullet
\end{array}$$

$$\begin{array}{c}
\bullet \\
\bullet$$

$$\begin{array}{c}
\bullet \\
\bullet$$

$$\begin{array}{c}
\bullet \\
\bullet
\end{array}$$

$$\begin{array}{c}
\bullet \\
\bullet$$

$$\begin{array}{c}
\bullet \\
\bullet
\end{array}$$

$$\begin{array}{c}
\bullet \\
\bullet$$

$$\begin{array}{c}
\bullet \\
\bullet$$

$$\begin{array}{c}
\bullet \\
\bullet$$

$$\begin{array}{c}
\bullet \\
\bullet
\end{array}$$

$$\begin{array}{c}
\bullet \\
\bullet$$

$$\begin{array}{c}
\bullet \\
\bullet$$

$$\begin{array}{c}
\bullet \\
\bullet
\end{array}$$

$$\begin{array}{c}
\bullet \\
\bullet
\end{array}$$

$$\begin{array}{c}
\bullet \\
\bullet$$

$$\begin{array}{c}
\bullet \\
\bullet
\end{array}$$

$$\begin{array}{c}
\bullet \\
\bullet$$

$$\begin{array}{c}
\bullet \\
\bullet
\end{array}$$

$$\begin{array}{c}
\bullet \\
\bullet$$

$$\begin{array}{c}
\bullet \\
\bullet
\end{array}$$

$$\begin{array}{c}
\bullet \\
\bullet
\end{array}$$

$$\begin{array}{c}
\bullet \\
\bullet
\end{array}$$

$$\begin{array}{c}
\bullet \\
\bullet$$

All steps are actually in equilibrium, but I only want you to show the forward direction

10. Provide reagents for the following transformations. (4 pt each)

11. Design a synthesis for the following alkene **FROM ALCOHOLS WITH NO MORE THAN 5 CARBONS**. (6 pt)

JASPERSE CHEM 360 TEST 3

**VERSION 3** 

Ch 18 Ketones and Aldehydes

Ch 22 Additions and Conensations of Enols and Enolate Ions

- 1. Physical Properties.
  - a. Rank the following according to <u>solubility in water</u>, 1 being most soluble, 4 being least soluble.

b. Rank the following according to boiling point, 1 being highest boiling, 4 lowest boiling.

c. Rank the following according to <u>equilibrium enol content</u>, 1 having the most and 3 the least enol.

d. Rank the following according to <u>acidity</u>, 1 being most acidic and 4 least acidic.

$$NO_2$$
  $NO_2$ 

- 2. <u>Nomenclature</u>. Provide Either the Name or the Structure for the Following Chemicals. (10 points)
- a. 3-propylbenzaldehyde
- b. (S)-3-phenylbutanal
- c. (Z)-2-methylhept-4-en-3-one

3. Identify the starting carbonyl compound or compounds from which the following aldol-type reaction products are formed. (12 points)

4. Draw the mechanisms for the following transformations.

5. Draw the products for the following reactions. (2 points each)

Br 
$$\frac{1. \text{ NaCN}}{2. \text{ PhMgBr}}$$
 3.  $\text{H}_3\text{O}^+$ 

6. Provide the needed reagents for the following transformations. You may use anything you wish. The transformations can be completed within 2-4 steps.

**JASPERSE** CHEM 360 TEST 4 **VERSION 1** 

Ch 19 Amines Ch 20 Carboxylic Acids

Ch 21 Carboxylic Acid Derivatieves

1. Synthesis Reactions. Draw the feature product of the following reactions. (3 pts each)

$$NH_2$$
 +  $Cat. H^+$ 

Ph Br 
$$\frac{1. \text{ KCN}}{2. \text{ H}_3\text{O}^+, \text{ heat}}$$

2. Draw the starting materials for the following hydrolysis reactions. (2 pts each)

- 3. a) Which one(s) of the following will react spontaneously with H<sub>2</sub>O? (2 pts)
- b) Which one(s) will react spontaneously with Me<sub>2</sub>NH? (2 pts) [Note: there may be more than one that reacts.]

4. Shown are two isomers. Circle the one with the higher boiling point. (2 points)

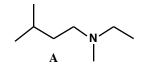
5. Provide Reagents for the Following Transformations (4 pts each)

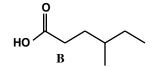
6. Name the Following or Draw the Structure (2 pts each)

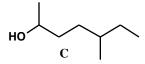
- b. N-methyl-N-ethyl-3-hexanamine
- c. methyl benzoate

7. Provide Mechanisms for the Following Reactions. (Note: In some cases, these may be "partial" reactions.) (16 points)

- 8. Which (if any) after being dissolved in diethyl ether, will: (4 points)
- a) Extract into NaOH/H<sub>2</sub>O?
- b) Extract into HCl/H<sub>2</sub>O?
- c) Extract into neutral water?







- 9. Of the following, which form would exist at: (4 points)
- a) pH = 2 (acidic)
- b) pH = 7 (neutral)
- c) pH = 12 (basic)



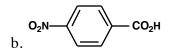




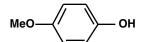


10. Rank the basicity of the three Nitrogen atoms, from most to least (1 most, 3 least). (2 pts)

- 11. Rank the acidity of the following, 1 being most acidic, 3 being least (2 pts each)
- a. ethanoic acid
- CH<sub>3</sub>NH<sub>3</sub>+Cl
- ethanol







- 12. Rank the following in order of increaing basicity (2 points each)
- a. NH<sub>3</sub>

- CH<sub>3</sub>NH<sub>2</sub>
- PhNH<sub>2</sub>

- b. NaOH
- CH<sub>3</sub>NH<sub>2</sub>
- sodium ethanoate

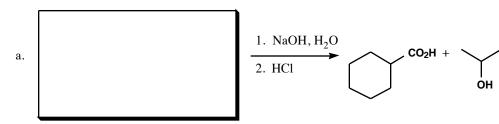
- c. NH
- NH

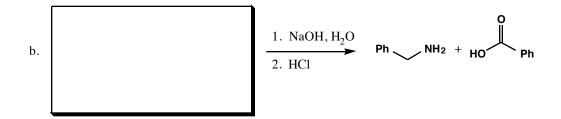
JASPERSE CHEM 360 TEST 4 VERSION 2 Ch 19-21 Amines, Carboxylic Acids, Carboxylic Acid Derivatives

1. Synthesis Reactions. Draw the feature product of the following reactions (need not show any byproducts). (22 points, 2 points each)

$$\begin{array}{c|c} \mathbf{O} & & \mathbf{H}_2\mathbf{N}\mathbf{M}\mathbf{e} \\ \hline & \mathbf{O}\mathbf{M}\mathbf{e} & \\ \end{array}$$

2. Hydrolysis Reactions. Draw the starting materials for the following hydrolysis reactions. (4 points)





3. Draw the <u>Mechanisms</u> for the following reactions. (16 points total. Some are relatively trivial, so point values will vary.)

4. Provide Reagents for the following Transformations (12 points)

- 5. Which (if any) after being dissolved in diethyl ether, will: (6 points. Note: The answers may be none or more than one, you tell me!)
- a) Extract into NaOH/H<sub>2</sub>O?
- b) Extract into HCl/H<sub>2</sub>O?
- c) Extract into water?

$$\bigcap_{A} OH \qquad \bigcap_{B} OH \qquad \bigcap_{C} NH_{2}$$

6. Nomenclature. Provide Either the Name or the Structure for the Following Chemicals. (8 points)

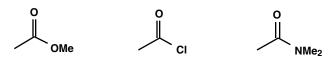
a. N-propyl-5-methylhexan-1-amine

b. (R)-2-bromopropanoic acid

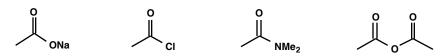
7. For each nitrogen a-d, identify the hybridization of the <u>nitrogen atom</u>, and identify the hybridization of the <u>nitrogen lone pair</u>. (6 points, 2 points off for 1st error, 1 for each additional)

| a N                                   | Nitrogen<br>Atom | Hybridization of the Nitrogen Atom | Hybridization of the Nitrogen Lone Pair |
|---------------------------------------|------------------|------------------------------------|---|
| N $N$ $N$ $N$ $N$ $N$ $N$ $N$ $N$ $N$ | <u>a</u>         |                                    |   |
| H c                                   | <u>b</u>         |                                    |   |
|                                       | <u>c</u>         |                                    |   |
|                                       | <u>d</u>         |                                    |   |

8. Rank the following according to their reactivity toward NaOH/ $H_2O$  hydrolysis, from 1 (most) to 3 (least). (2 points)



9. Circle the compounds, if any, (may be none, one, or more than one) that would  $\underline{not}$  react with methanol to give a methyl ester: (4 points)



10. Rank the acidity of the following, 1 being most acidic, 3 being least (9 points)

a. CH<sub>3</sub>NH<sub>3</sub>+Cl<sup>-</sup> benzoic acid water

b. CH<sub>3</sub>CO<sub>2</sub>H CH<sub>3</sub>CH<sub>2</sub>OH CH<sub>3</sub>CH<sub>2</sub>NH<sub>2</sub>

c. water p-nitrobenzoic acid p-methylbenzoic acid

11. Rank the basicity of the following, 1 being most basic, 3 being least (9 points)

a.  $PhNH_2$  (CH<sub>3</sub>)<sub>3</sub>N CH<sub>3</sub>NH<sub>2</sub>

b. Me<sub>2</sub>NH CH<sub>3</sub>CO<sub>2</sub>Na H<sub>2</sub>O

c. NaOH CH3MgBr pyridine

JASPERSE CHEM 360 TEST 4 VERSION 3 Ch 19-21 Amines, Carboxylic Acids, Carboxylic Acid Derivatives

- 1. Nomenclature. Provide Either the Name or the Structure for the Following Chemicals. (10 points)
- a. N-ethyl-N-methyl-4-methylpentan-1-amine
- b. sodium (R)-3-hydroxybutanoate
- c. 5-amino-4-methylpentanoic acid

$$f \sim 0$$

2. For each nitrogen a-f, identify the hybridization of the <u>nitrogen atom</u>, and identify the hybridization of the <u>nitrogen lone pair</u>. [Adenine is an important player in information transfer (DNA, RNA, genetics, etc.) and energy storage/release (ATP/ADP).]

$$\begin{array}{c} H & e & NH_2 \\ a & N & d \\ h & c \end{array}$$

| Nitrogen | Hybridization of  | Hybridization of       |
|----------|-------------------|------------------------|
| Atom     | the Nitrogen Atom | the Nitrogen Lone Pair |
|          |                   |                        |
| <u>a</u> |                   |                        |
|          |                   |                        |
| <u>b</u> |                   |                        |
|          |                   |                        |
| <u>c</u> |                   |                        |
| d        |                   |                        |
| <u>u</u> |                   |                        |
| <u>e</u> |                   |                        |
| _        |                   |                        |
| f        |                   |                        |

3. Synthesis Reactions. Draw the feature product of the following reactions (need not show any byproducts). (15 points)

c. 
$$\frac{1. \text{ LiAlH}_4}{2. \text{ H}_3\text{O}^+}$$

d. OH 
$$\frac{1. \text{ SOCl}_2}{2. \text{ Me}_2\text{NH (excess)}}$$

$$3. \text{ LiAlH}_4; \text{H}_2\text{O}$$

e. 
$$\frac{\text{MeNH}_2, \text{cat. H}^+}{\text{NaBH}_3\text{CN}}$$

4. Synthesis Reactions. Draw the feature product of the following reactions (need not show any byproducts). (15 points)

a. HO 
$$\rightarrow$$
 OH  $\rightarrow$  Cat.  $\rightarrow$  H

d. 
$$O$$
OH
 $1. SOCl_2$ 
 $2. MeOH$ 

5. Draw the mechanisms for the following reactions. (5 points)

6. Provide Reagents for the following Transformations (15 points)

- 7. Which, when dissolved in diethyl ether, will: (5 points each)
- a) Extract into NaOH/H<sub>2</sub>O?
- b) Extract into HCl/H<sub>2</sub>O?
- c) Extract into water?

$$A$$
 $Me_2N$ 
 $B$ 
 $C$ 
 $D$ 

8. Hydrolysis Reactions. Draw the starting materials for the following hydrolysis reactions. (6 points)

a. 
$$\frac{1. \text{ NaOH, H}_2\text{O}}{2. \text{ HCl}} \xrightarrow{\text{CO}_2\text{H} + \text{HO}} \frac{\text{CO}_2\text{H} + \text{HO}}{\text{Ph}}$$
b. 
$$\frac{1. \text{ NaOH, H}_2\text{O}}{2. \text{ HCl}} \xrightarrow{\text{Ph}} \frac{\text{CO}_2\text{H} + \text{HO}}{\text{CO}_2\text{H} + \text{HO}} \xrightarrow{\text{CO}_2\text{H}} \frac{\text{CO}_2\text{H}}{\text{Ph}} = \frac{\text{CO}_2\text{H}}{\text{CO}_2\text{H}} + \frac{\text{CO}_2\text{H}}{\text{CO}_2\text{H}} = \frac{\text{CO}_2\text{H}}{\text{CO$$

9. Rank the following according to their reactivity toward NaOH/H<sub>2</sub>O hydrolysis.

Given the structures **A-D** above, which of the following reactions will proceed spontaneously? (2 points)

$$A + H_2NCH_3 \rightarrow B$$
  
 $A + HOCH_3 \rightarrow C$ 

 $A + HCl \rightarrow D$ 

10. Rank the acidity of the following, 1 being most acidic, 3 being least (3 points each)

- a. acetic acid vs. water vs. NH<sub>4</sub>+Cl-
- b. CH<sub>3</sub>OH vs. CH<sub>3</sub>NH<sub>2</sub> vs. F<sub>2</sub>CHOH
- c. p-methoxybenzoic acid vs. benzoic acid vs. acetone

- 11. Rank the basicity of the following, 1 being most basic, 3 being least (3 points each)
- a. CH<sub>3</sub>OH vs. PhNH<sub>2</sub> vs. CH<sub>3</sub>NH<sub>2</sub>

b. 
$$v_{S}$$
.  $v_{S}$ .  $v_{S}$ .

c. 
$$(CH_3CH_2)_3N$$
  $H_2O$ 

a.

e.

1. Give the major product for the following reactions. (3 points each)

$$\begin{array}{c} \text{O} \\ \text{H} \\ \hline \\ \text{O} \\ \text{O} \\ \end{array} \begin{array}{c} \text{1. CH}_3\text{OH, H}^+ \\ \hline \\ \text{2. NaBH}_4\text{, CH}_3\text{OH} \\ \text{3. H}_2\text{O, H}^+ \\ \end{array}$$

$$g. \begin{picture}(200,0) \put(0,0){\line(1,0){100}} \put(0,0){\line(1,0)$$

$$k$$
.

$$\begin{array}{ccc}
& & & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
& & & \\
&$$

$$\begin{array}{c} \text{1.} \ \ \text{H}_2\text{CrO}_4 \\ \text{2.} \ \ \text{SOCl}_2 \\ \hline \\ \text{3.} \ \ \text{CH}_3\text{CH}_2\text{NH}_2 \\ \text{(plus NaOH base)} \end{array}$$

#### 2. Provide the **mechanisms** for the following reactons (3 points each)

a. 
$$\begin{array}{c} O \\ O \\ \hline O \\ \hline \end{array}$$
 1. LiAlH<sub>4</sub>  $\begin{array}{c} O \\ \hline \end{array}$  HO  $\begin{array}{c} O \\ \hline \end{array}$  OH

e.

f. O 1. BrMg OH OH 2. 
$$H_3O^+$$

3. Give **Names or structures** for the following: (6 points)

4. <u>Separatory Funnel/Extraction</u>: Suppose the following three chemicals are initially dissolved in ether in a separatory funnel. (2 points each; there will not necessarily be something extracted in each aqueous wash, so "none" might be the correct answer. ).

$$H_2N$$
 $A$ 
 $B$ 
 $O$ 
 $C$ 

- a. Identify which (if any) would <u>extract out into the aqueous layer</u> if treated with <u>basic</u> water (NaOH/ $H_2O$ ).
- b. Identify which (if any) would <u>extract out into the aqueous layer</u> if treated with <u>acid water</u> (HCl/H<sub>2</sub>O).
- c. Identify which (if any) would <u>extract out into the aqueous layer</u> if treated with <u>neutral</u> <u>distilled water  $(H_2O)$ .</u>
- 5. Mystery Problems: Suggest a structure for an unknown A whose formula is  $C_6H_{12}O_2$  and gives the following chemical test results. (4 points)

• Formula  $C_6H_{12}O_2$ 

• Hydrogenation Test H<sub>2</sub>/Pt No reaction

• Chromic Acid Test H<sub>2</sub>CrO<sub>4</sub> Reacts, turns green/brown, precipitate forms.

Lucas Test
 HCl/ZnCl<sub>2</sub>
 Reacts, makes 2<sup>nd</sup> layer.
 2,4-DNP Test
 2,4-dinitrophenylhydrazine
 Reacts, yellow precipitate

Tollens Test Ag(NH<sub>3</sub>)<sub>2</sub> OH No reaction
 Iodoform Test excess I<sub>2</sub>, NaOH, H<sub>2</sub> No reaction

• H-NMR: 4.5 (1H, broad s), 3.9 (1H, sextet), 2.7 (2H, d), 2.3 (2H, q), 1.1 (3H, d), 1.0 (3H, t)

#### 6. Rank the following, with 1 being highest, or most. (2 points each)



$$\downarrow \uparrow \downarrow 0$$

Reactivity towards nucleophilic attack (for example, by PhMgBr)

a.

b.

**Boiling Point** 

H<sub>0</sub>N ^

Water Solubility

c.

$$d. \begin{picture}(20,0) \put(0,0){\line(1,0){100}} \put(0,0){\line(1,0){$$

$$\downarrow \downarrow \downarrow c$$

Reactivity towards nucleophilic attack

### 7. Rank the acidity of the following, from 1 (most) to 4 (least): (4 pts)

H<sub>2</sub>O

# 8. Rank the basicity of the following, 1 being most basic, 3 being least

a.



CH<sub>3</sub>NH<sub>2</sub>

b.

CH<sub>3</sub>NHNa

CH<sub>3</sub>C(O)NH<sub>2</sub>

 $(CH_3)_3N$ 

## 9. Of the following, which one form would exist under basic conditions? (ex, pH = 10)

$$\bigvee_{A}^{\bigoplus} O^{\bigcirc}$$

$$NH_2$$
 $B$ 
 $O$ 

$$\bigvee_{C}^{NH_2} OH$$

$$\bigvee_{D}^{\bigoplus} OH$$

- 10. Provide the reagents necessary to accomplish the following transformations (4 points each). You may use anything you wish, as big as you like.
  - Note 1: Real test will have 6 problems of this type, but I included more for practice

$$\begin{array}{c} O \\ H \\ \end{array} \longrightarrow \begin{array}{c} O \\ Ph \\ \end{array}$$

e.

11. Retrosynthesis: Design syntheses of the following. (4 points each). Allowed starting materials include <u>alcohols with ≤5 carbons</u>; and any inorganic reagents (PCC, H<sub>2</sub>CrO<sub>4</sub>, PBr<sub>3</sub>, PPh<sub>3</sub>, BuLi, Mg, etc.)

12. Put in the starting materials for the following. (Note: May be only one chemical in several of these cases). (2 points each)

a.

b.

c.

$$\xrightarrow{H^+} \bigcirc \bigcirc \bigcirc \bigcirc$$

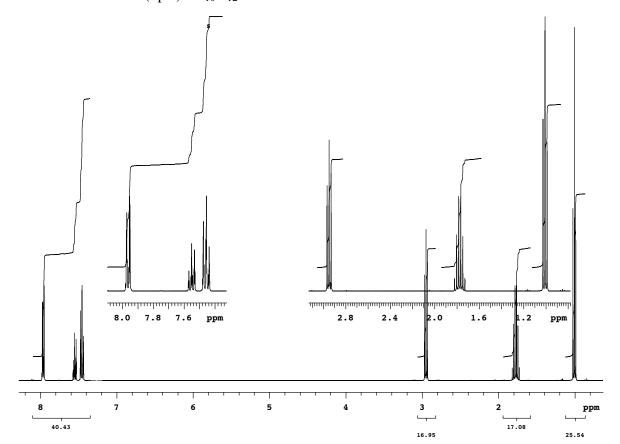
d.

13. Predict the 1H NMR spectrum. Include the source (CH<sub>3</sub>-1, etc); approximate chemical shifts (1's, 2's, etc.); integration (1H, 2H, etc.); and splitting (either list the number of lines, or else use letters: "s" for singlet; "d" for doublet etc.). If signals are symmetry equivalent, do not list them twice. (5 pts)

Source Chem Shift Integration Splitting

 $\begin{array}{c|c}
3 & 0 & 5 & 7 \\
1 & 0 & 6 & 7
\end{array}$ 

14. Solve the structure (7pts):  $C_{10}H_{12}O$  IR = 1680



11. Solve structure (7 pts):  $C_6H_{12}O_2$  IR: 1745  $^{13}C$ : 170(s), 70(t), 28(d), 21(q), 19(q)

