Practice Tests Answer Keys, Organic Chemistry 2

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

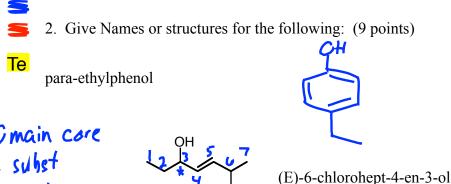
1. Give the major product for the following reactions. (3 points each)

$$\begin{array}{c|c}
\text{H_OH} & 1. \text{ Na} \\
\hline
\text{alc} & 2 \\
\hline
\end{array}$$

$$\begin{array}{c}
\text{Br} \\
\end{array}$$

$$\begin{array}{c}
\text{SN2} \\
\end{array}$$

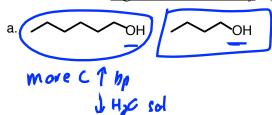
$$\begin{array}{c}
\text{ether} \\
\end{array}$$



3-methy1-2-propyl-1-pentanol

3-methyl-3-propylpentan-1-ol

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 higher water solubility. (4 points)



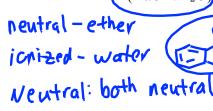
4. Which of the following statements is **true**? (4 points)

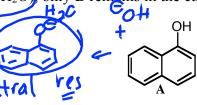
When an ether solution of **A** and **B** in a separatory funnel is treated with neutral water, only $\mathbf{R}_{+\mathbf{A}}$ remains in the ether layer.

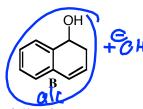
When an ether solution of **A** and **B** in a separatory funnel is treated with neutral water, neither **A** nor **B** remains in the ether layer.

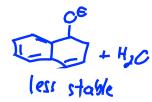
c. When an ether solution of A and B in a separatory funnel is treated with basic water (NaOH/H₂O), both **A** and **B** remain in the ether layer.

d. When an ether solution of A and B in a separatory funnel is treated with basic water (NaOH/H₂O), only **B** remains in the ether layer.









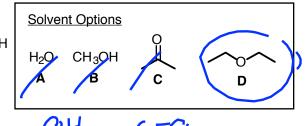
5. For the following transformation, which of the following statements is true? (4 points)

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



6. Suggest a possible structure for an unknown A whose formula is $C_5H_{10}O$ and gives the following chemical test results. (5 points)

Formula
Hydrogenation Test
Chromic Acid Test
Lucas Test

 $\begin{array}{l} C_5H_{10}O \\ H_2/Pt \\ H_2CrO_4 \\ HCl/ZnCl_2 \end{array}$

EU=1

No reaction
Turns Green
Reacts within 5 minutes

CH

OH

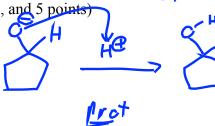
7. Provide the mechanisms for the following reactons (3, 5, and 5 points)

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

not C=C

HE Add

Add



C Add (3) Add

OH H-Br Me Me Add

OH H-Br Me

Obrav all
intermediates

(2) Brav all
formal charges

(3) Brav all arrows

(4) No backwards
arrows

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

Ph OH

$$OH$$
 OH
 OH
 OH
 OH
 OH
 OH
 OH
 OH
 OH

Te

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 any esters ethylene oxide formaldehyde iodomethane any acyclic alcohol or alkene wth \(\leq 4 \) carbons

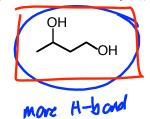
any "inorganic" agents (things that won't contribute carbons to your skeleton)

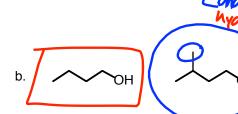
VERSION 2

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

ortho-chlorophenol

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





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

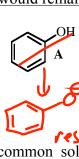


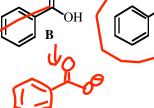


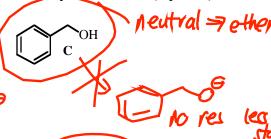




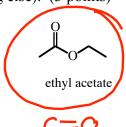
4. If an ether solution of the following three compounds was washed with NaOH/H₂O, which (if any) of the compounds would remain in the ether layer? Circle any that would. (3 points)

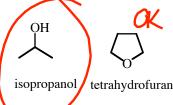






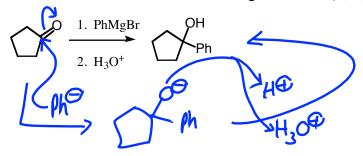
Of the following common solvents, circle those that are unsuitable as solvents for the preparation and reactions of Grignard reagents (assuming you want the Grignard reagent to react with something else). (3 points)

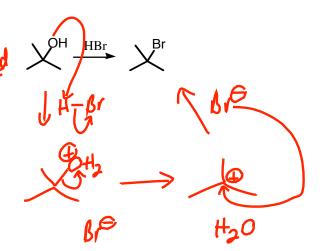


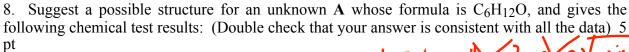


6. Give the major product of the following reactions. (3 points each)

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







Formula: $C_6H_{12}O$ EU all e? $C_6H_{12}O$ H_2/Pt No reaction H_2CrO_4 Turns green $C_6H_{12}O$ $C_6H_{12}O$



9. Provide reagents for the following transformations. ("workup" means H₃O⁺ or H₂O steps) (First two are 3 points each; last four are 5 points each)



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

cyclopentanol any acyclic alcohol or alkene with ** carbons

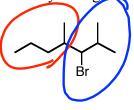
any esters

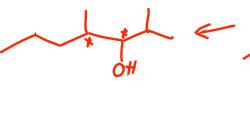
ethylene oxide

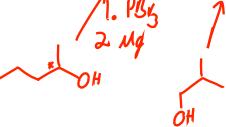
formaldehyde (CH₂O)

iodomethane

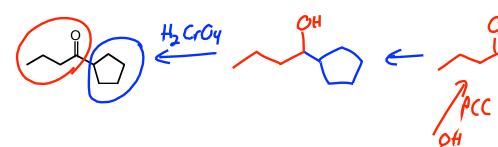
any "inorganic" agents (things that won't contribute carbons to your skeleton)

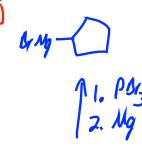
















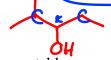
JASPERSE CHEM 360 TEST 1 Reactions involving Alcohols



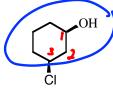
1. 2-Methylpentan-3-ol)s classified as: (3 points)

a. a primary alcohol b. a secondary alcohol

c. a tertiary alcohol d. none of the above

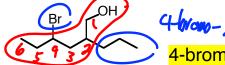


2. Provide acceptable names for the following: (10 points total)

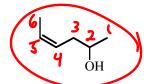


cis-3-chlorocyclohexand

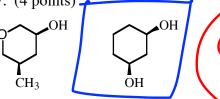
racemic



4-bromo-2-propylhexan-1-ol



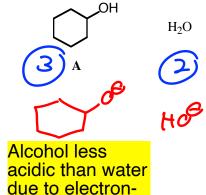
3. Circle he molecule with the highest boiling point. Put a square around the molecule with the highest water solubility. (4 points)



Extra C's raises bp

Max H-bonding, min C's ideal for water.

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.



donating effect of

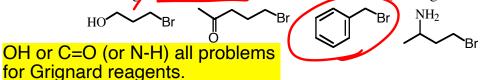
the alkyl group

CH₄
B (1) (4)

Phenols or acids are more acidic than water due to resonance stabilization

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

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



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

8. Draw a possible structure for an achiral molecule \mathbf{A} with formula $C_5H_{12}O$, given that when H_2CrO_4 is added to \mathbf{A} the solution turns green, and that the Lucas test with \mathbf{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)

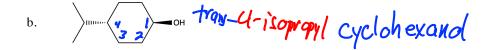
10. Design syntheses of the following, starting from alcohols of ≤4 carbons. (7 points each)

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



CH2CH3 4-ethylphend

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

CH₃NH₂

OH

(CH₃)₂CHOH

H₂O

H₂O

H₃O

H₃O

H₃O

H₄O

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

a. + NaOH

move

stable

b. OH + NaOH

Reschance

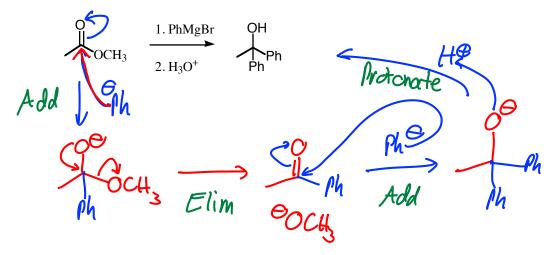
Stabilized

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

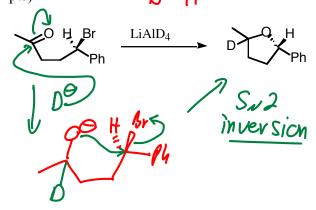
d. OMe
$$\frac{1. \text{ LiAlH}_4}{2. \text{ H}_3\text{O}^+}$$

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

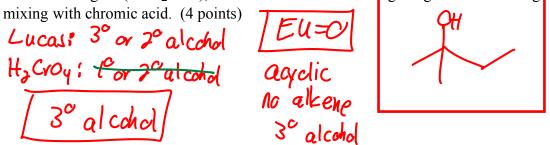
6. Draw the mechanism for the following reaction. (6 points)



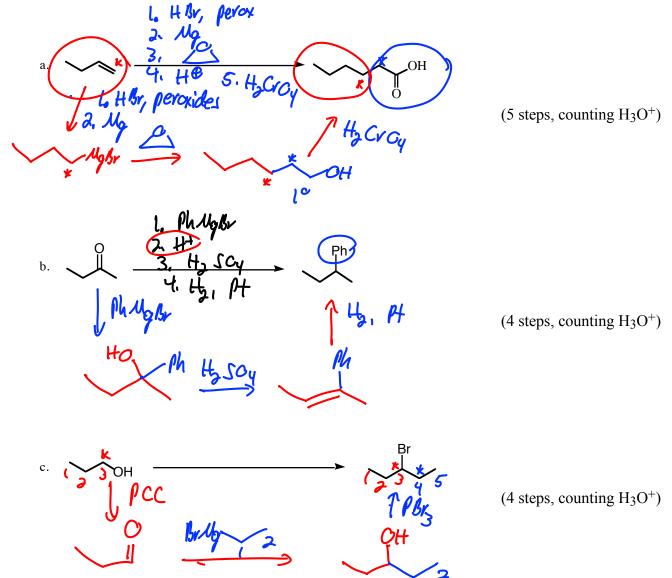
7. Draw the mechanism for the following reaction. Note: This is a slight twist on familiar stuff. The overall transformation appears unfamiliar, but the individual steps are actually familiar. (6 pts) Q = H



8. Suggest a structure for a compound "A" whose formula is $C_5H_{12}O$, that reacts instantly with the Lucas reagent (ZnCl₂/HCl), but does not cause an orange to green color change upon



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)



cycle extend

Yer log extend

Provide a synthesis for the following molecules. Permissible starting materials include

cyclopentanol, acyclic alcohols or alkenes of ≤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.)

Chem 360-Jasperse

1. Predict the ¹H NMR spectrum. Include the source (CH₃-1, 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	Splitting of lines
	CH3-a	2'1	GH	d 2
a, i	CH-b	2's	14	septet 7
° C de	CHz-C	3's (lau 4's)	24	+ 3
a a	CH2-d	1's	24	pentet 5
	CH2-e	211	24	sextet 6
	CH3-f	1'5	34	+ 3

2. Predict the ¹³C 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
О ОН	C1	50-0	G
	C2	220-160	- ^U S
2 6	C3	160-100	d
3 5 7	C4	220-160 160-100 160-100 50-0 100-50	d
	C5	50-0	+
	C6	100-50	d
	C7	50 - 0	8
			<u> </u>

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

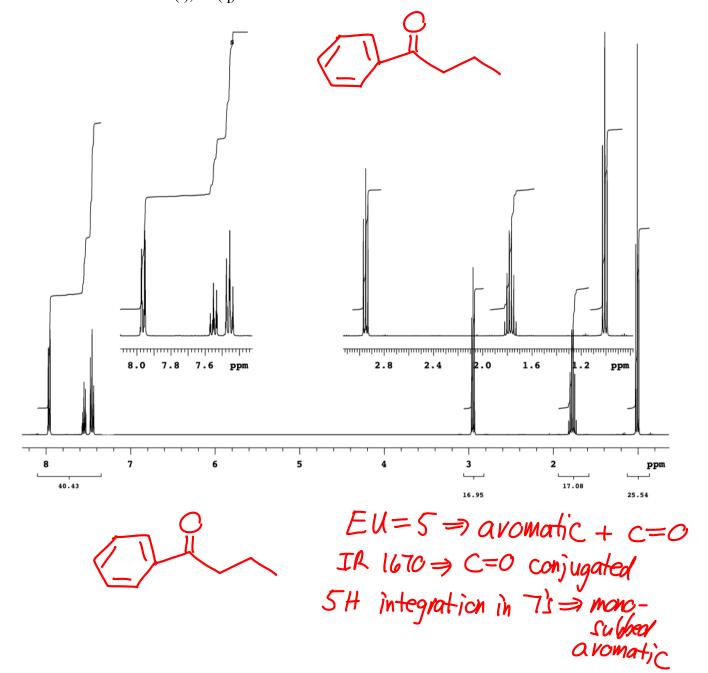
3) 2200 **A**

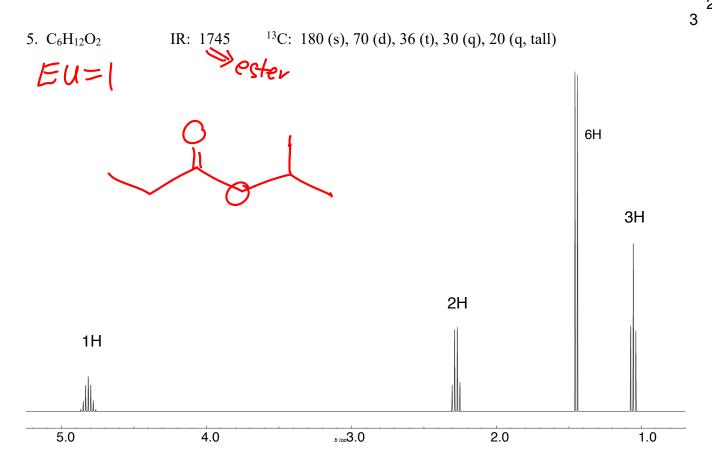
4) 1710

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. C₁₀H₁₂O IR: 1670

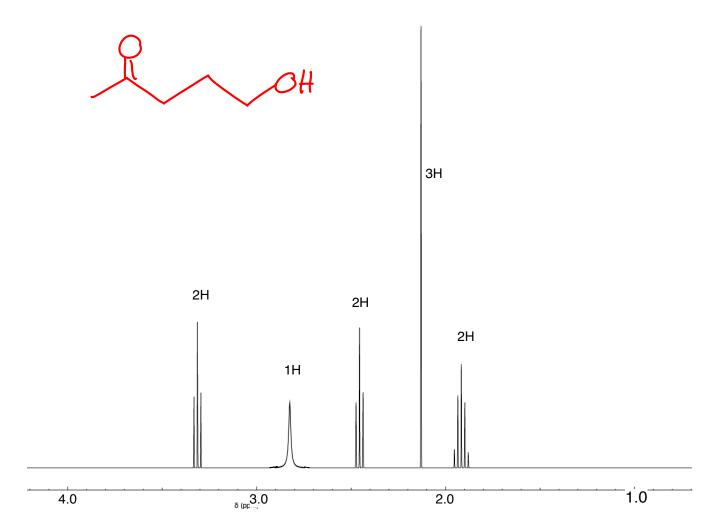
¹³C NMR: 210 (s, short), 150 (s, short), 130 (d, tall), 124 (d, tall), 120 (d), 33 (t), 26 (t), 20 (q)



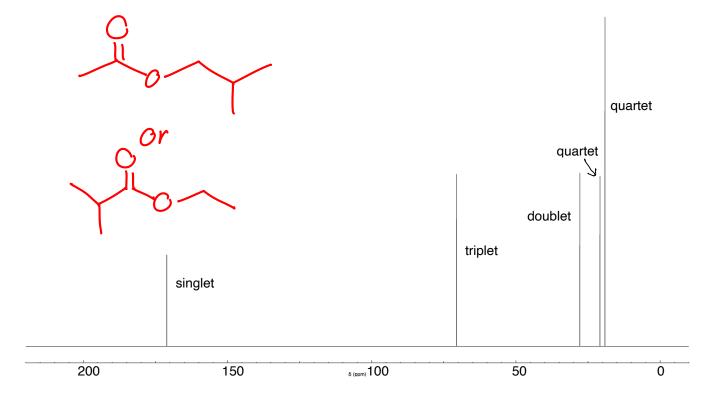


6. C₅H₁₀O₂

IR: 3300-3200, 1710 **Letone**13C: 210 (s), 65 (t), 38 (t), 35 (t), 28 (q)

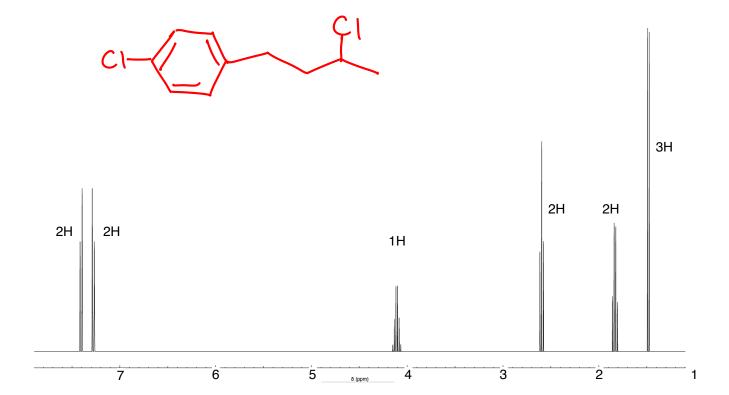


- The spectrum displayed is a "decoupled" 13-C NMR spectrum. (No splitting)
- But beside each coupled peak is a label that tells whether the carbon would be a singlet, doublet, triplet, or quartet **if** a "coupled" 13-C NMR had been obtained.
- (Note: There are two plausible solutions to this problem)



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

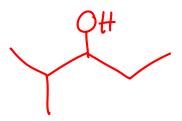
¹³C: 150 (s), 144 (s), 133 (d), 126 (d), 58 (d), 37 (t), 32 (t), 22 (q)



9. C₆H₁₄O 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

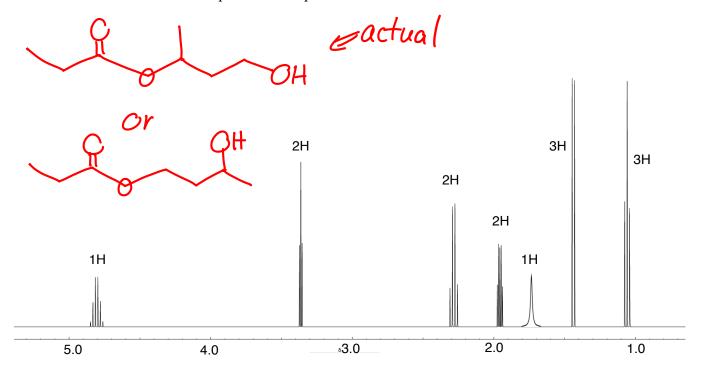


10. C₇H₁₄O₃

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

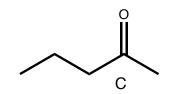
Predict the ¹H NMR spectrum. Include the source (CH₃-1, etc); approximate chemical shifts (1's, 2's, etc.); integration (1H, 2H, etc.); and splitting (either list the number of lines, or else use letters: "s" for singlet; "d" for doublet etc.). If signals are symmetry equivalent, do not list them twice.

$a \rightarrow d$ $c \leftarrow fg$	Source CH3-a CH3-b CH-C CH3-d CH3-e CH-f	Chem Shift 1's 2's 2's 1's 3's 3's	Integration 3H 2H 1H 3H 2H 1H	Splitting 3 = + 4 & 6 mult. 2 d 7 mult.
	CH-f CH3-g	2 ¹ 2	1H 6H	7 mult. 2 d

2. Predict the ¹³C 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).

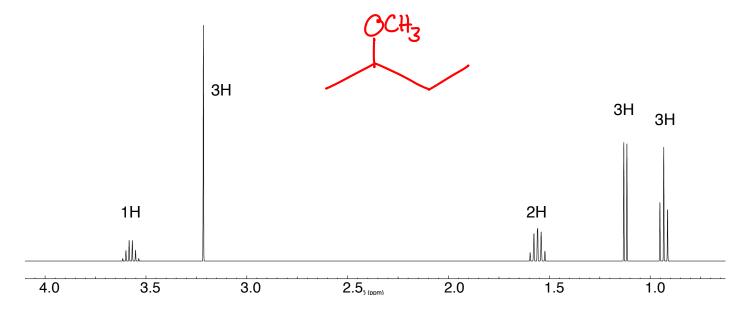
	Source	Approximate Chem Shift	Splitting
) 	C1	220-160	2
	C2	160-100 160-100 100-50	d
0 1 2	C3	160-100	S
4 //3	C4	100-50	+
	C5	50-0	Q
5			0

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



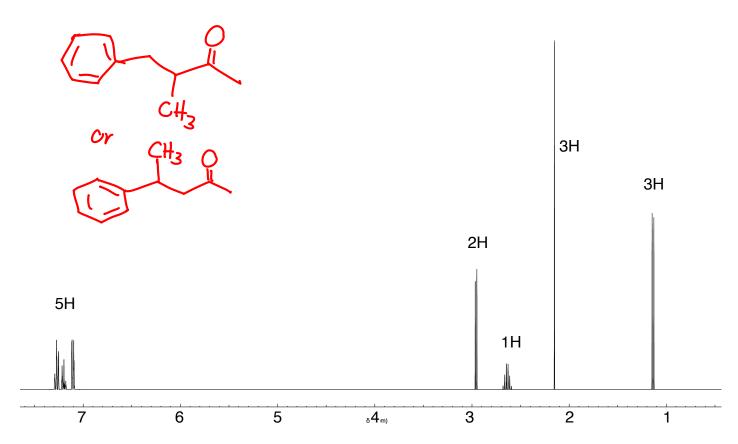
For the remainder of the test, solve the structures for the following. If you get a structure perfect, you will get full credit. If you do not get a structure perfect, you may still get some partial credit. Thus, it is in your interest to show some of you work, make a structure, or tell me what you know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

4. C₅H₁₂O IR: Nothing interesting



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

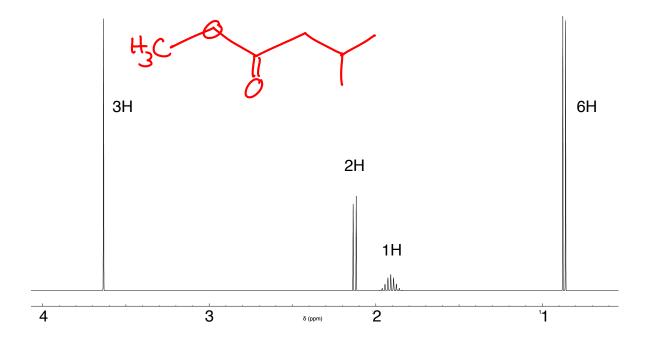
• (Note: There are two plausible solutions to this problem)

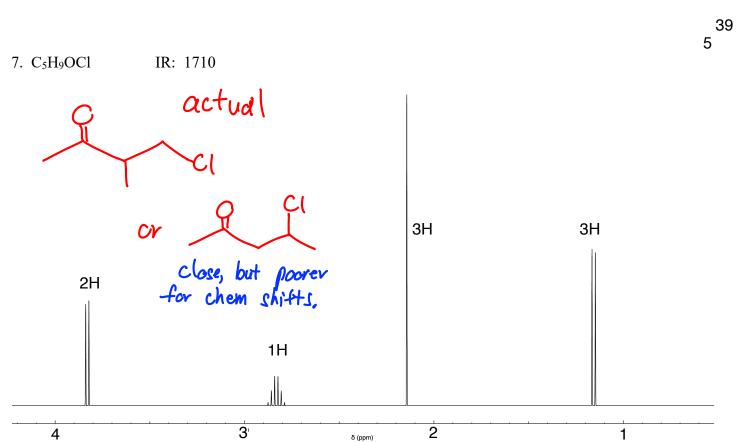


6. C₆H₁₂O₂

IR: 1745

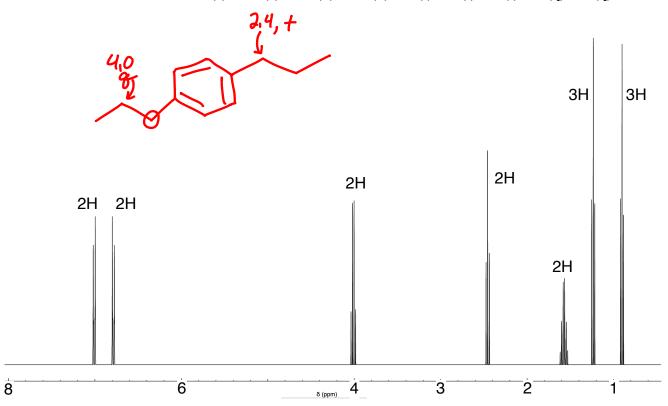
¹³C: 170 (s), 65 (q), 42 (t), 37 (d), 18 (q)





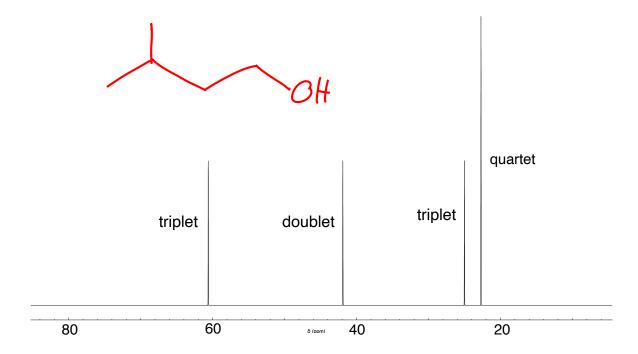
 $C_{11}H_{16}O$ 8.

IR: Nothing interesting ¹³C: 148 (s), 140 (s), 130 (d), 125 (d), 64 (t), 38 (t), 25 (t), 15 (q), 14 (q)



9. C₅H₁₂O

- 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.

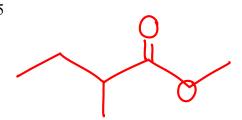


0.92, 3H, triplet 1.12, 3H, doublet

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.

Chem 360-Jasperse Test #2 NMR, IR

Version 3.

Predict the ¹H NMR spectrum. Include the source (CH₃-1, 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	Splitting
91	CH3-a	13	6H	2 = d
· · · · · · · · · · · · · · · · · · ·	CH-6	25	114	7 = m
b	CH-C	7'5	2H	2 d
á	CH-d	215	211	2 d
	CHz-e	212	2H	4 %
d o f	CHf	1/5	3#	3 4
	् उ			

2. Predict the ¹³C 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	0-50	8
	C2	220-160	S
$\frac{1}{2}$	C3	100-50	+
1 6	C4	50-0	+
	C5	50-0	+
	C6	160-100 160-100	d
	C7	160-100	+
	1	1	1

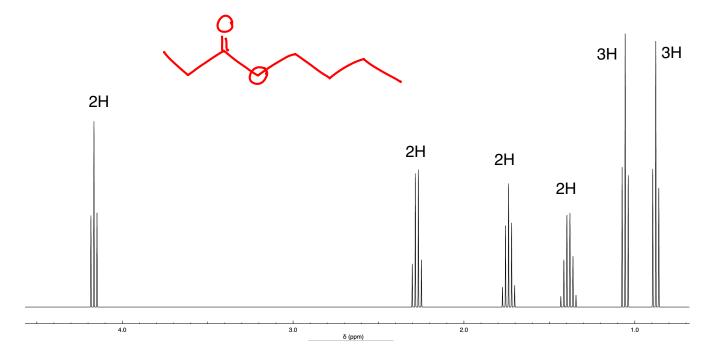
3. Match the following structures with the listed feature IR signals. (Write the letter of the structure by the IR signal):

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.

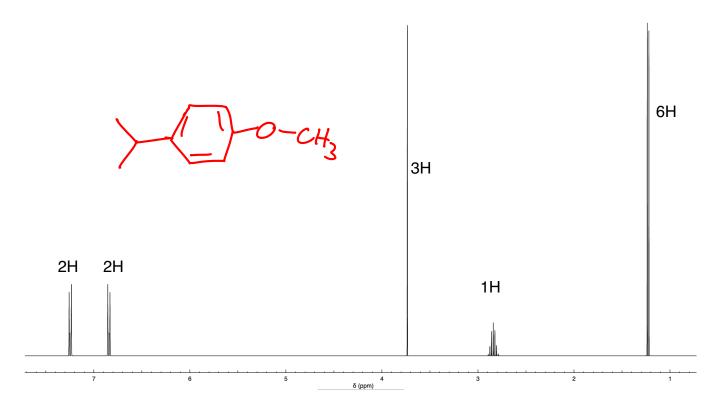
4. C₇H₁₄O₂

IR: 1745

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



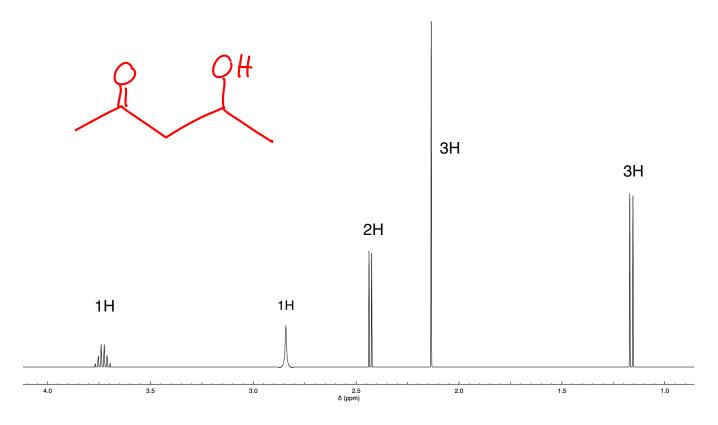
¹³C: 158 (s), 141 (s), 128 (d), 114 (d), 65 (q), 33 (d), 24 (q, tall)



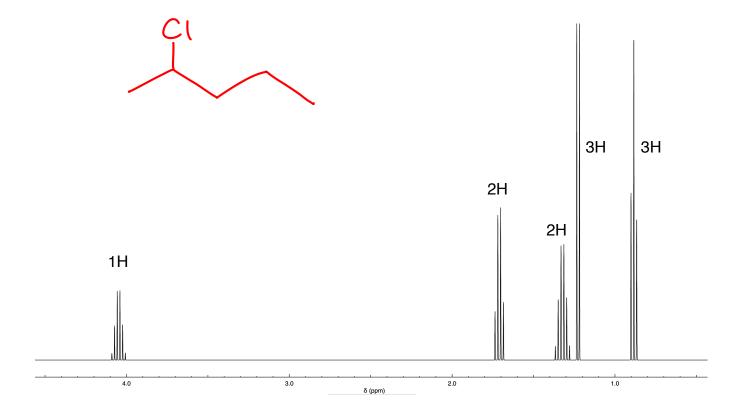
6. C₅H₁₀O₂

IR: 3300-3200, 1710

¹³C: 210 (s), 65 (d), 40 (t), 30 (q), 23 (q)



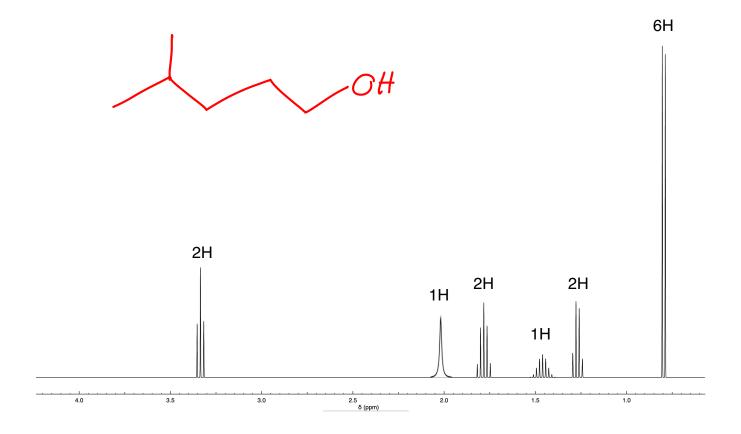
7. C₅H₁₁Cl



8.

C₆H₁₄O IR: 3300-3200

¹³C: 63 (t), 34 (t), 30 (t), 27 (d), 22 (q, tall)



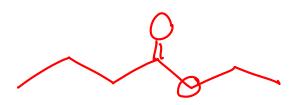
9. C₆H₁₂O₂ IR: 1745

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

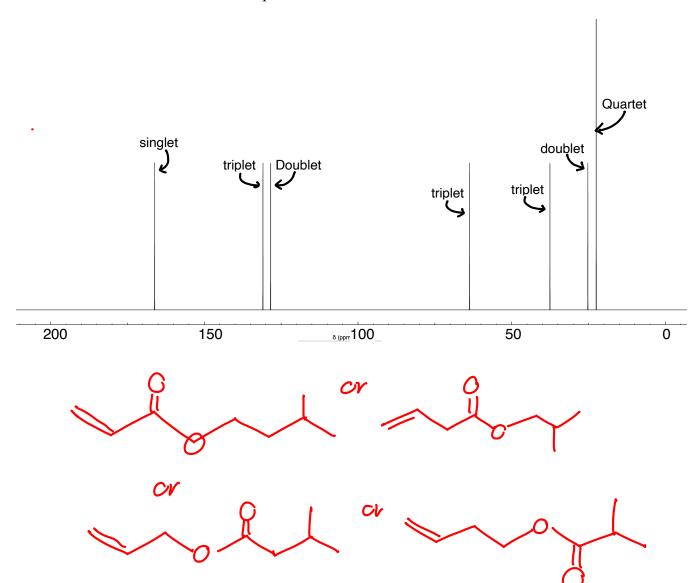
2.22, 2H, triplet

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.

Chem 360-Jasperse Test #2

NMR, IR

Version 4.

Predict the ¹H NMR spectrum. Include the source (CH₃-1, 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.

, 0	<i>J</i> 1		
Source	Chem Shift	Integration	Splitting
CH2-1	2's	34	1= s
CH3-2	3/2	24	3 +
CH2-3	1'5	7 H	5 pents
CH2-4	21/5	ンル	6 sextet orn
CH3-5	13	34	3 +
	Source CH3-1 CH3-2 CH3-3 CH3-4	Source Chem Shift CH3-1 CH3-2 CH3-3 CH3-4 I'S	Source Chem Shift Integration CH3-1 2's 3H CH3-2 3's 2H CH3-3 1's 2H CH3-4 1's 2H

2. Predict the ¹³C 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
O	C1	50-0	9
	C2	220-160	Š
$\frac{1}{2}$ $\frac{4}{5}$ $\frac{6}{5}$	СЗ	100-50	+
1 2 0 3 5	C4	50-0	+
	C5	50-0	+
	C6	50-0	8

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

1) 3300-3400 2) 1745	C B	O	OCH ₃	ОН
3) 1710	A	A	В	C

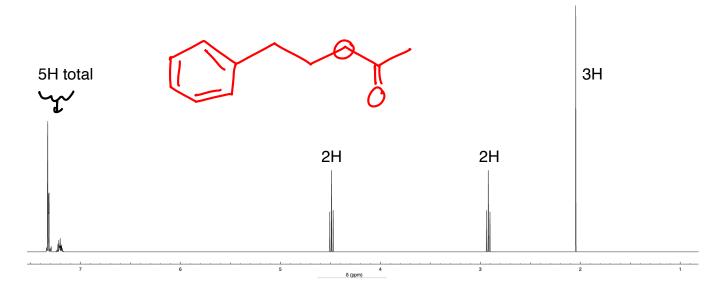
4. Match the dimethyl benzene isomer for which the ¹³C NMR spectrum has:.

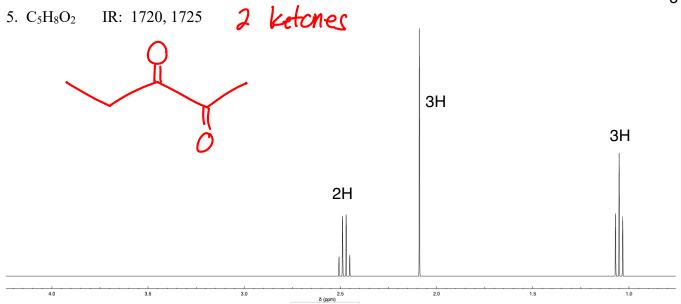
For the remainder of the test, solve the structures for the following. If you get a structure perfect, you will get full credit. If you do not get a structure perfect, you may still get some partial credit. Thus, it is in your interest to show some of you work, make a structure, or tell me what you know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

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

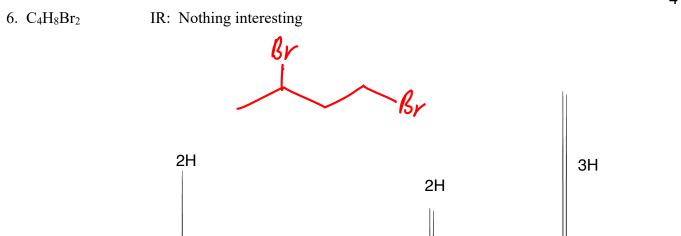
IR: 1745

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







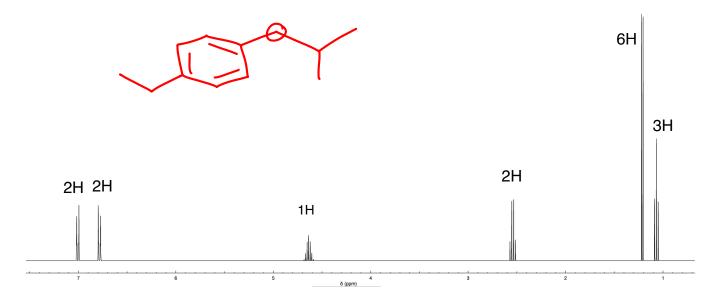


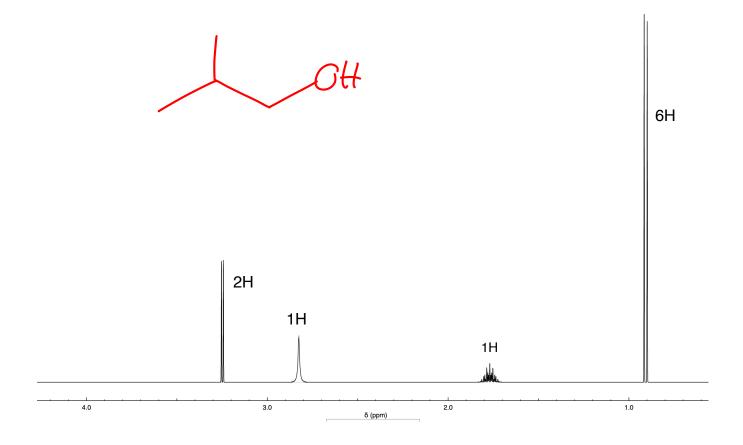
1H

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

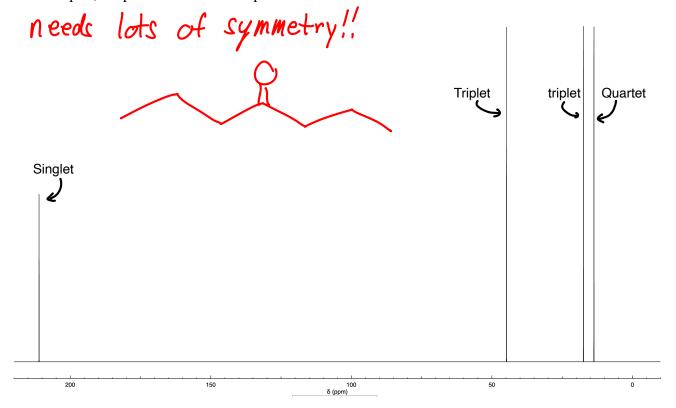
IR: nothing interesting

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



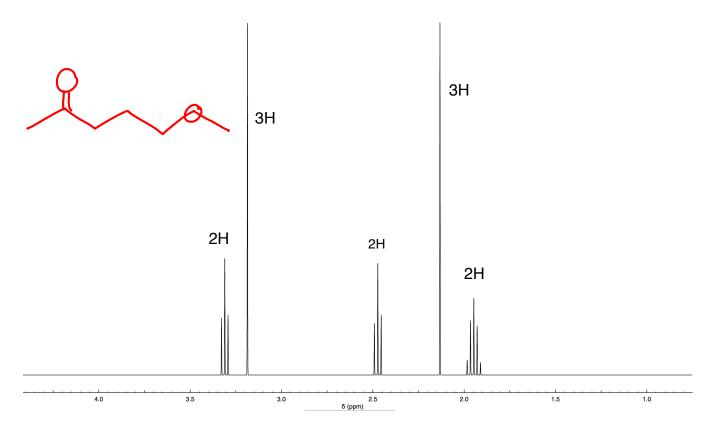


- 9. C₇H₁₄O
- IR: 1710
- The spectrum displayed is a "decoupled" 13-C NMR spectrum. (No splitting)
- But beside each coupled peak is a label that tells whether the carbon would be a singlet, doublet, triplet, or quartet **if** a "coupled" 13-C NMR had been obtained.



10. $C_6H_{12}O_2$

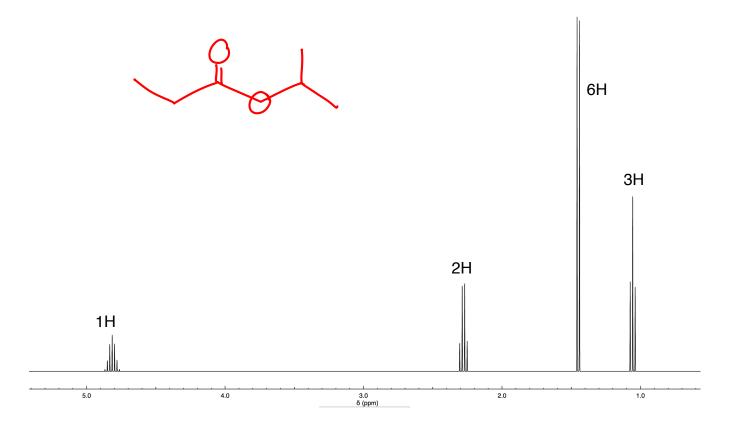
IR: 1710 13C-NMR: 210 (s), 75 (t), 65 (q), 40 (t), 30 (t), 20 (q), 20 (q)



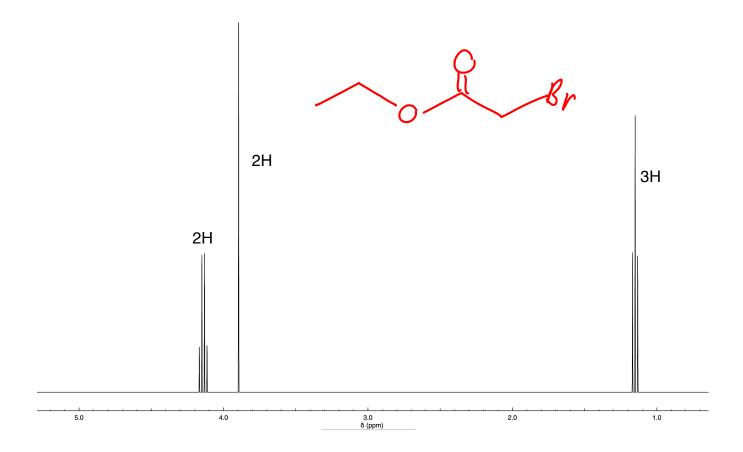
11. $C_6H_{12}O_2$

IR: 1745

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



11. C₄H₇O₂Br IR: 1745



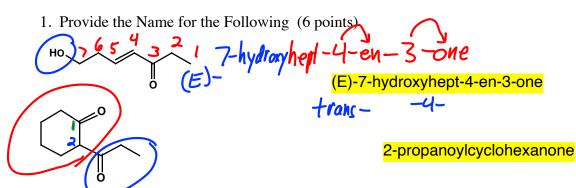
• I have not, accidentally or intentionally, seen copies or parts of the test in advance, including online. In the event that I did, I will report this to the instructor as soon as possible.

JASPERSE CHEM 360 TEST 3

VERSION 1

Ch 18 Ketones and Aldehydes

Ch 22 Additions and Conensations of Enols and Enolate Ions



2. Of the following structures,

Which will be "completely" (>98%) deprotonated by LDA (LiN-iPr₂)? (2 points) A, B, C

LDA deprotonates mono carbonyls

Which will be "completely" (>98%) deprotonated by NaOH? (2 points)

the H NMR (incomplete) is a 6H doublet at 1.2 ppm. What is X? (4 points)

Oxyanion => dicarbonyls

(PNR)

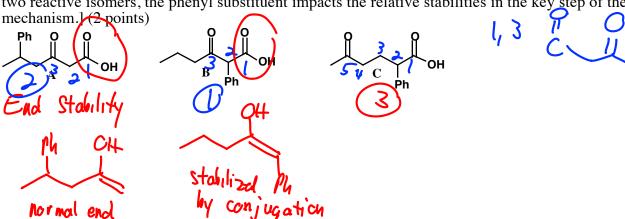
3. An unknown **X** has formula C₄H₈O. It gives 1) an orange precipitate upon treatment with 2,4-dinitrophenylhydrazine (2,4-DNP) and it gives 2) a silver mirror upon treatment with Tollen's reagent [Ag(NH₃)₂+OH⁻]. 3) It does not react with Br₂ in dichloromethane solvent. 4) Included in

DNP C=0 isompy | H C-H3

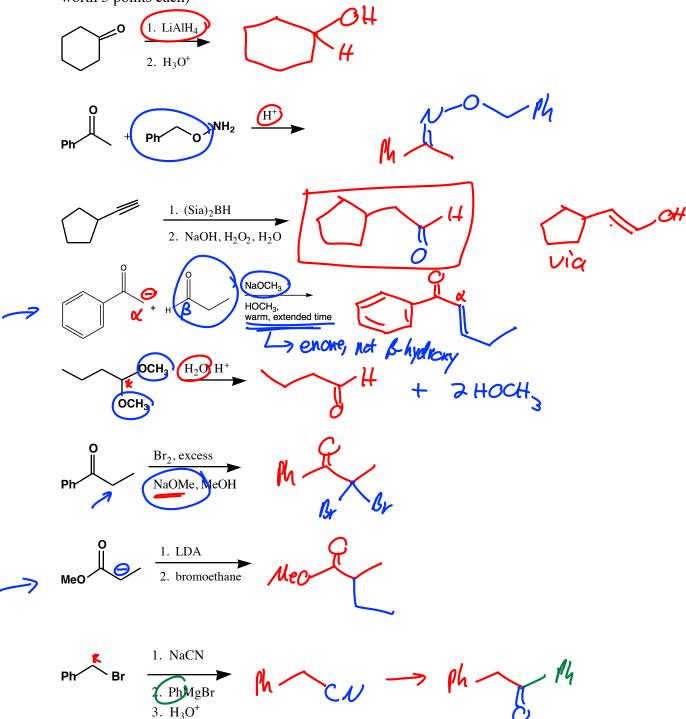
Aldehyde not ketone

No ring

4. Rank the rate of decarboxylation (loss of CO₂) 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

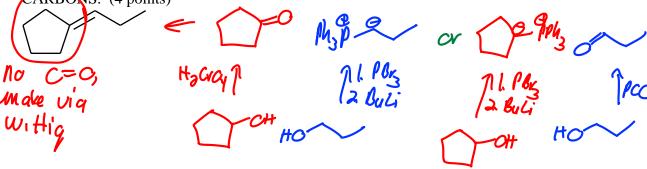


5. Synthesis Reactions. Draw the feature product of the following reactions (need not show any byproducts). NOTE: In every case, the product should be a stable, isolable **product**; an "intermediate" structure will not receive full credit. (2 or 3 points each; 1st 7 worth 2 points; last 5 worth 3 points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

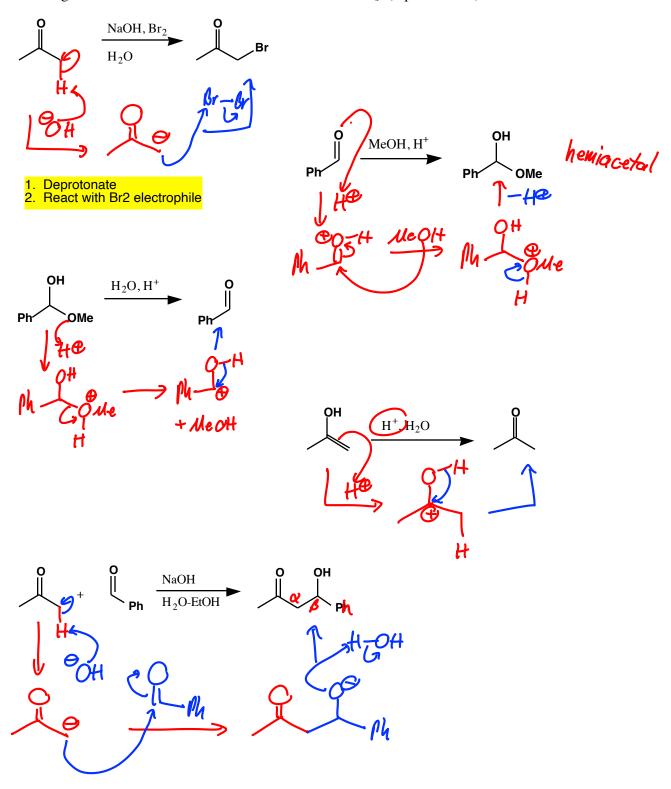


7. Put in the starting materials from which the following structures would be produced. Depending on the product, the appropriate starting material may be either a single molecule, two of the same molecule, or two different molecules. For the last problem, you are required to start from two separate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

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)



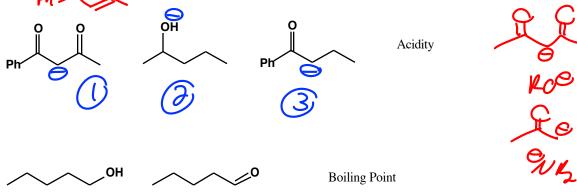
10. Rank the following, with 1 being highest, or most. (2 points each)

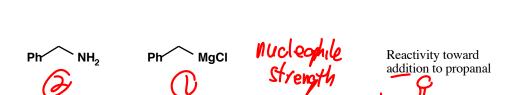
Relative amount in the "enol" form at equilibrium

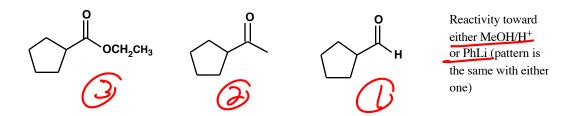
Can make a stabilized enol

No alpha-H, no enol possible

Acidity







Aldehyde > ketone > ester

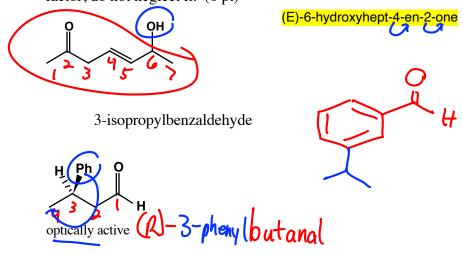
JASPERSE CHEM 360 TEST 3



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)

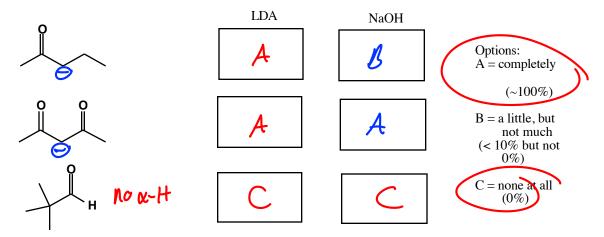


2. Rank the following, with 1 being highest, or most. (6 pt)

Carbonyl reactant:
1. Addition acidic?
2. Addition anionic?
3. Enolate Anionic 3. Draw the products for the following reactions (3 pt each) KCN, HCN Products must be isolable, stable Markov NaOMe, MeOH NaOEt, EtOH NaOMe MeOH

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

5. For the following chemicals, describe the extent to which each would be deprotonated by LDA (LiN-iPr₂) 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/I2, the iodoform test methy cerone
- c. It does not react with Tollen's reagent [Ag(NH₃)₂+OH-].
- d. It does not react with Br₂ in dichloromethane solvent.
- e. Chemical formula is C7H12O 16-D=4H short 2 EU
- f. It's ¹³C spectrum shows 5 carbons (1 singlet, 1 doublet, 2 triplets, and 1 quartet)

7. Which of the following would not undergo decarboxylation (loss of CO₂) 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)

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

11. Design a synthesis for the following alkene FROM ALCOHOLS WITH NO MORE

JASPERSE CHEM 360 TEST 3

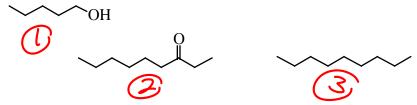


Ch 18 Ketones and Aldehydes

Ch 22 Additions and Conensations of Enols and Enolate Ions

1. Physical Properties.

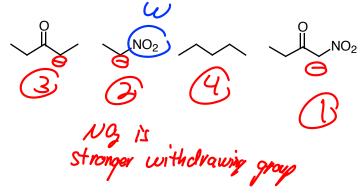
a. Rank the following according to solubility in water, 1 being most soluble, 4 being least soluble.



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

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

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



2. <u>Nomenclature</u>. Provide Either the Name or the Structure for the Following Chemicals. (10

points)

- a. 3-propylbenzaldehyde
- H
- b. (S)-3-phenylbutanal

- Ph H
- c (Z) 2-methyl-4-hepten-3-one
- d. (HO)H
 (S)-4-hydroxy hexan-3-one
- e. Brit (1)-3-hromo Cyclopentanone
- 3. Identify the starting carbonyl compound or compounds from which the following aldol-type reaction products are formed. (12 points)

a. M H

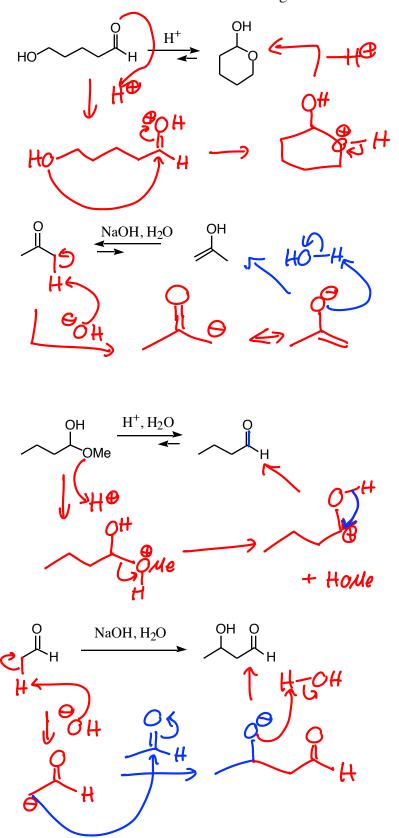
b. Ph

c.



NaOMe, MeOH

4. Draw the mechanisms for the following transformations.



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

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

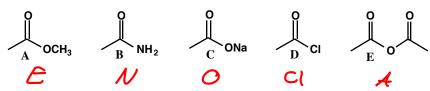
VERSION 1 **JASPERSE CHEM 360** TEST 4 Ch 19 Amines Ch 20 Carboxylic Acids

Ch 21 Carboxylic Acid Derivatieves

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

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_2O ? (2 pts) \int_{0}^{∞}
- b) Which one(s) will react spontaneously with Me₂NH? (2 pts) 0, 5, A [Note: there may be more than one that reacts.]



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

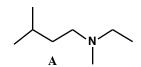
5. Provide Reagents for the Following Transformations (4 pts each)

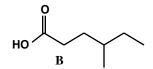
6. Name the Following or Draw the Structure (2 pts each)

- 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/H₂O?
- b) Extract into HCl/H₂O?
- c) Extract into neutral water?
- none





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



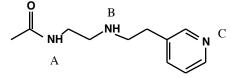








10. Rank the basicity of the three Nitrogen atoms, from most to least (1 most, 3 least). (2 pts)





- 11. Rank the acidity of the following, 1 being most acidic, 3 being least (2 pts each)
- a.
- ethanoic acid
- CH₃NH₃⁺Cl⁻

ethanol



CO₂H

ОН

Donor/Withdrawer factor

2. RCO2H > phenol

- 12. Rank the following in order of increasing basicity (2 points each)
- a.

- PhNH₂

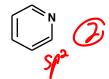


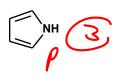


CH₃NH₂

sodium ethanoate







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)

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

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

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/H₂O? Hydroxide ionize/extra acids or phenols
- b) Extract into HCl/H₂O? HCl/Water ionized/extracts amines
- c) Extract into water?

 Neutral water doesn't ionize any

$$\bigcap_{A} OH \qquad \bigcap_{B} OH \qquad \bigcap_{C} NH_2$$

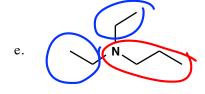
6. Nomenclature. Provide Either the Name or the Structure for the Following Chemicals. (8 points)

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

$$CH = CH$$

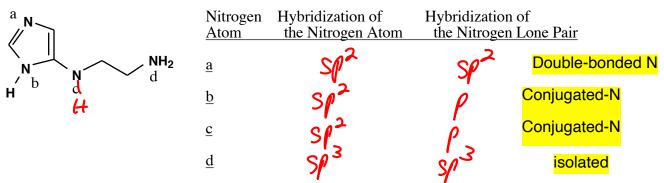
b. (R)-2-bromopropanoic acid

3-hydroxy pentanoic acid

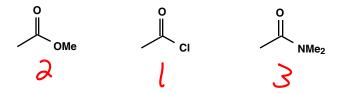


N, N-diethyl propan-l-amine

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)



8. Rank the following according to their reactivity toward NaOH/H₂O hydrolysis, from 1 (most) to 3 (least). (2 points)



CI A E N O	metha	anol to give a n	ONa Peach	ny, (may be not of the points) (4 points) co co would React downholl llowing, 1 being	Not re	Pez)	would React South!	not react with	•
	a.	CH ₃ NH ₃ +C	1-	benzoic acid	water			amine	
	b.	CH ₃ CO ₂ H) ~e	CH ₃ CH ₂ OH	CH ₃ Cl	H ₂ NH ₂	e NH	HOE	
	c.	water 3	p-nitrol	penzoic acid	p-meth	nylbenzoic a	cid		
	11. R	Rank the basici	ty of the fo	ollowing, 1 bein	ng most basic,	3 being leas	st (9 points)		
	a.	PhNH ₂		(CH ₃) ₃ N	D	CH ₃ NH ₂	2		
	b.	Me ₂ NH		CH ₃ CO ₂ Na		H ₂ O			
	c.	NaOH	CH ₃ M ₄		pyridir QM				

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 PH C
- c. 5-amino-4-methylpentanoic acid

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

$H_{\stackrel{\circ}{N}} \sim NH_2$	Nitrogen Atom	Hybridization of the Nitrogen Atom	Hybridization of the Nitrogen Lone Pair
a _N N d	<u>a</u>	sp ²	Sp ²
N N	<u>b</u>	3p2	ρ
	<u>c</u>	s p2	S/2
	<u>d</u>	sp2	Sp
	<u>e</u>	spa	
	<u>f</u>	. Sp3	Sp3

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

a. Ph Br
$$\frac{1. \text{ Mg}}{2. \text{ CO}_2}$$
 $\frac{\text{CO}_2}{3. \text{ H}^+}$

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

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

d.
$$\begin{array}{c} \begin{array}{c} \begin{array}{c} 1. \text{ SOCl}_2 \\ \hline \\ \text{OH} \end{array} \end{array} \begin{array}{c} \begin{array}{c} 1. \text{ SOCl}_2 \\ \hline \\ 2. \text{ Me}_2 \text{NH (excess)} \end{array} \end{array}$$

e.
$$\frac{\text{MeNH}_{2, \text{cat.}} \text{H}^{+}}{\text{NaBH}_{3}\text{CN}}$$

$$\frac{\text{MeNH}_{2, \text{cat.}} \text{H}^{+}}{\text{NaOH, H}_{2}}$$

$$\frac{1. \text{ NaOH, H}_{2}}{2. \text{ H}^{+}}$$

$$\text{HOCH}_{3}$$

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

a. HO
$$\frac{1}{4}$$
 $\frac{1}{1}$ $\frac{1}{1}$

d.
$$\frac{1. \text{ SOCl}_2}{2. \text{ MeOH}}$$

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/H₂O? A

NaOH ionizes RCO2H and phenols

- b) Extract into HCl/H₂O?
- B

HCI ionizes amines

c) Extract into water?

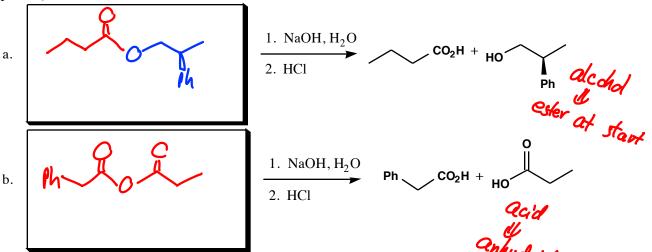


Neutral water does not ionize them

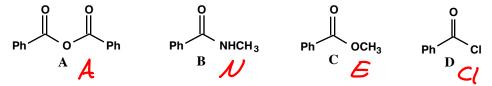
$$A$$
 Me_2N B

$$C$$
 D

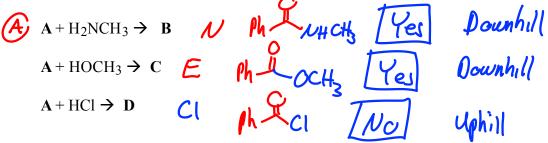
8. Hydrolysis Reactions. Draw the starting materials for the following hydrolysis reactions. (6 points)



9. Rank the following according to their reactivity toward NaOH/H₂O hydrolysis.



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

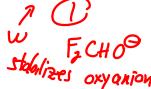


- 10. Rank the acidity of the following, 1 being most acidic, 3 being least (3 points each)
- acetic acid a.
- VS. water
- NH₄+Cl-VS.





- b. CH₃OH
- CH₃NH₂ VS.
- F₂CHOH VS.



- p-methoxybenzoic acid c.
- VS.
- benzoic acid





- 11. Rank the basicity of the following, 1 being most basic, 3 being least (3 points each)
- a.
- CH₃OH
- VS.
- PhNH₂
- CH₃NH₂ VS.



VS.

- c.
- $(CH_3CH_2)_3N$

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

d.

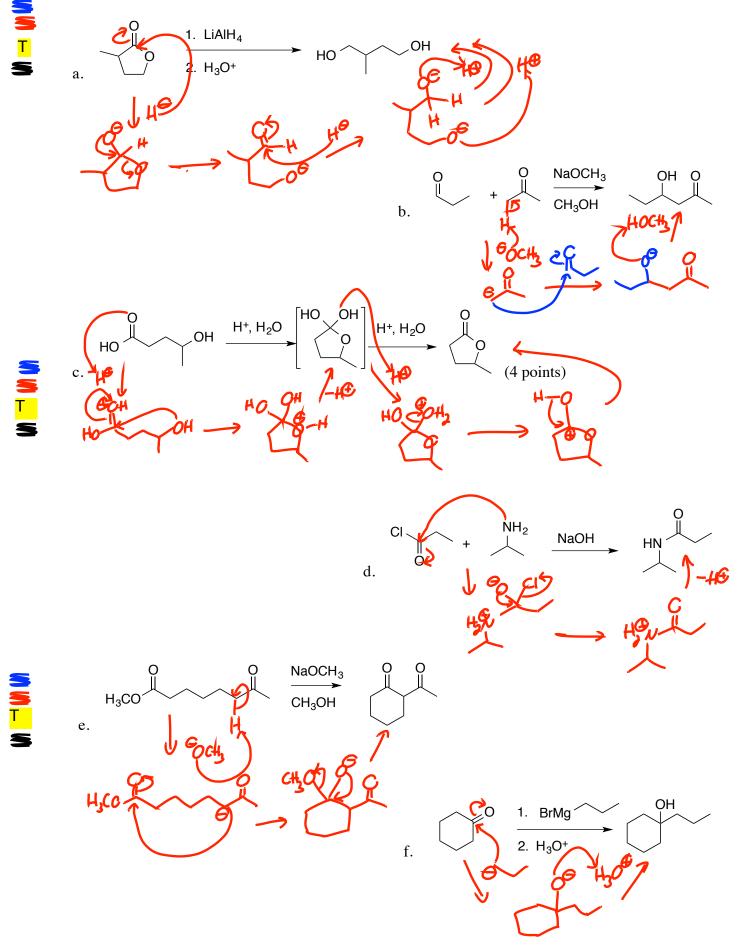
e.

$$\stackrel{\text{H}}{\longrightarrow} 0$$
NaBH₃CN, H⁺

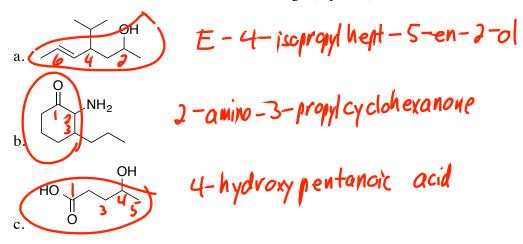
$$m$$
. H_2O, H^+

$$OH \xrightarrow{\begin{array}{c} 1. \ H_2CrO_4 \\ 2. \ SOCl_2 \\ \hline \\ 3. \ CH_3CH_2NH_2 \\ \text{(plus NaOH base)} \end{array}}$$

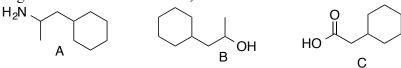
2. Provide the **mechanisms** for the following reactons (3 points each)



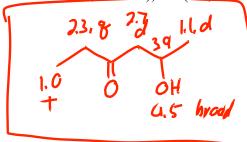
3. Give Names or structures for the following: (6 points)

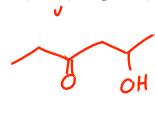


4. <u>Separatory Funnel/Extraction</u>: Suppose the following three chemicals are initially dissolved in ether in a separatory funnel. (2 points each; there will not necessarily be something extracted in each aqueous wash, so "none" might be the correct answer.).

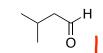


- a. Identify which (if any) would <u>extract out into the aqueous layer</u> if treated with <u>basic</u> water (NaOH/ H_2O).
- b. Identify which (if any) would <u>extract out into the aqueous layer</u> if treated with <u>acid water</u> (<u>HCl/H₂O</u>).
- c. Identify which (if any) would extract out into the aqueous layer if treated with neutral distilled water $(\mathbf{H}_2\mathbf{O})$.
- 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 $C_6H_{12}O_2$ | EU Hydrogenation Test H_2/Pt no alkene No reaction Chromic Acid Test H₂CrO₄ Reacts, turns green/brown, precipitate forms. Lucas Test HCl/ZnCl₂ Reacts, makes 2nd layer. Reacts, yellow precipitate 2,4-DNP Test 2,4-dinitrophenylhydrazine Tollens Test $Ag(NH_3)_2^+OH^-$ No reaction **Iodoform Test** excess I₂, NaOH, H₂ 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)



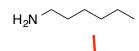
OCH₃

Reactivity towards nucleophilic attack (for example, by PhMgBr)

b. 0 3

Boiling Point

a.



но ~~~

HO 3

Water Solubility

c.

Reactivity towards nucleophilic attack

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

H₂O

b. 0 0

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

a



CH₃NH₂

b.

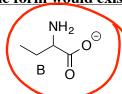
CH₃NHNa

CH₃C(O)NH₂

 $(CH_3)_3N$

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





$$\begin{array}{c}
\oplus\\ NH_3\\ D\\ O\end{array}$$

c.

e.

- 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

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, H₂CrO₄, PBr₃, PPh₃, 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)

$$\frac{1. \text{ NaOH, H}_2\text{O}}{2. \text{ HCI}} \quad \text{HO} \qquad + \quad \text{H}_2\text{N}$$

a.

Note: Starting Material includes a ring, and has the formula $C_7H_{12}O_2$

c.

d.

	<u>Source</u>	Chem Shift	<u>Integration</u>	<u>Splitting</u>
1 0 5 6 7	CH3-1	21	34	3 +
1 - 0	CH2-2	2'5	24	4 8
	CH2-4	4'5	2 H	1 2
	CH 2-5	3'5	24	3 +
	CH2-6	21	24	6 septet
	CH3-7	2')	3 H	3 +

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

