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/

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

$$\underbrace{\overset{O}{\longleftarrow}}_{2. \text{ H}_3\text{O}^+} \underbrace{\overset{1. \qquad MgBr}{}_{2. \text{ H}_3\text{O}^+}}$$

Ph
$$\rightarrow$$
 OH $\xrightarrow{\text{H}_2\text{CrO}_4}$

$$\underbrace{\overset{O}{\longrightarrow}}_{\text{OCH}_3} \underbrace{\overset{1. \text{ PhMgBr (excess)}}{2. \text{ H}_3\text{O}^+}}$$

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

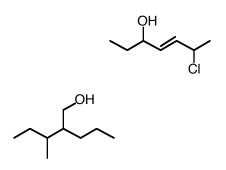
$$\underbrace{HOH}_{2.} \xrightarrow{\text{Br}}$$

$$\begin{array}{c} 1. \text{ PBr}_3 \text{ } 3. \text{ PhCHO} \\ \hline 2. \text{ Mg} \text{ } 4. \text{ } \text{H}_3\text{O}^+ \end{array}$$

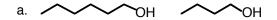
3

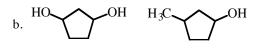
2. Give Names or structures for the following: (9 points)

para-ethylphenol

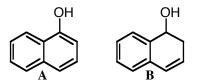


3. For each of the following pairs, <u>circle</u> the one that is <u>higher boiling</u> and put a <u>square</u> around the one with the <u>higher water solubility</u>. (4 points)

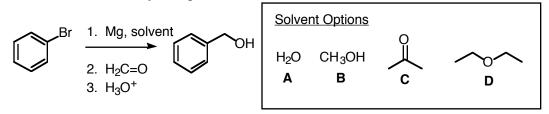




- 4. Which of the following statements is <u>true</u>? (4 points)
- a. When an ether solution of **A** and **B** in a separatory funnel is treated with neutral water, only **B** remains in the ether layer.
- b. When an ether solution of **A** and **B** in a separatory funnel is treated with neutral water, 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/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.



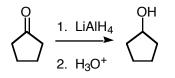
- 5. For the following transformation, which of the following statements is true? (4 points)
- a. **D** is the only acceptable solvent
- b. C is the only acceptable solvent
- c. C and D are both acceptable solvents
- d. **B**, **C**, and **D** are all acceptable solvents
- e. A and B are the only acceptable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

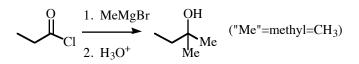


2

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)

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







3

Ph Br Ph Ph OH Ph OH (2-3 steps)(2-3 steps) ►ОН -QH (2 steps) optically active optically active $\xrightarrow{O}_{Ph} \xrightarrow{O}_{OH} (4-5 \text{ steps})$

Ph OH -

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

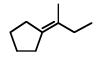
4

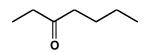
9. Rank the acidity of the following, from most acidic (1) to least acidic (4). (4 points)

H₂O OH ОН

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)



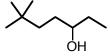


5

JASPERSE TEST 1 CHEM 360 Alcohols and Retrosynthesis

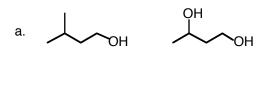
1. Give Names or structures for the following: (9 points)

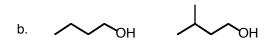
ortho-chlorophenol





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)

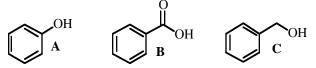




3. Of the listed four chemicals, circle those which would ionize methanol (convert it to sodium or magnesium methoxide)? (4 points)

Na NaNH₂ NaOH CH₃MgBr

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)



5. 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)

diethyl ether

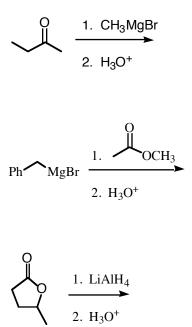
ethyl acetate

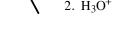
isopropanol tetrahydrofuran

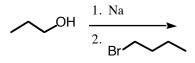
OН

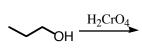
1

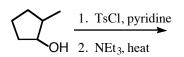
6. Give the major product of the following reactions. (3 points each)

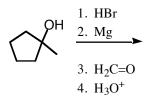




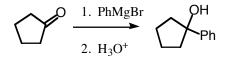




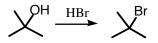




7. Draw mechanisms for the following reactions. (3, 5, and 5 points)



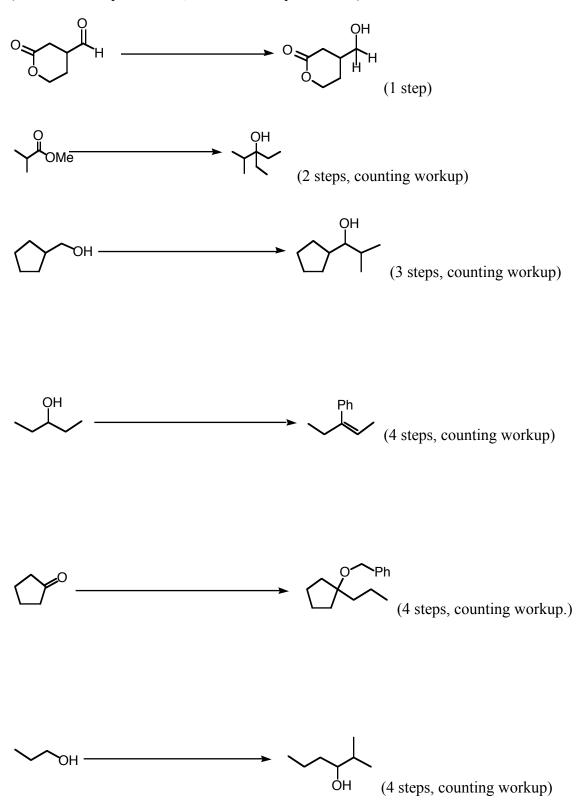
Ph OMe
$$\xrightarrow{1. \text{ LiAlH}_4}$$
 Ph OH
2. H₃O⁺ Ph OH



8. Suggest a possible structure for an unknown 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

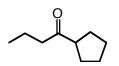
Formula:	$C_6H_{12}O$	
Hydrogenation Test	H ₂ /Pt	No reaction
Chromic Acid Test	H ₂ CrO ₄	Turns green
Lucas Test	HCl/ZnCl ₂	No reaction

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)



 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 6 points each of up to 5 carbons, not limited to only 4.
 whylene oxide formaldehyde (CH₂O) iodomethane any "inorganic" agents (things that won't contribute carbons to your skeleton)

Вr

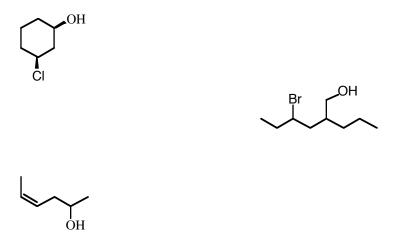


JASPERSE CHEM 360 TEST 1 VERSION 3 Reactions involving Alcohols

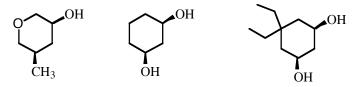
1. 2-Methyl-3-pentanol is classified as: (3 points)

a. a primary alcohol b. a secondary alcohol c. a tertiary alcohol d. none of the above

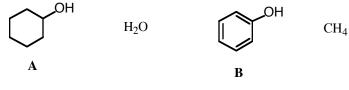
2. Provide acceptable names for the following: (10 points total)



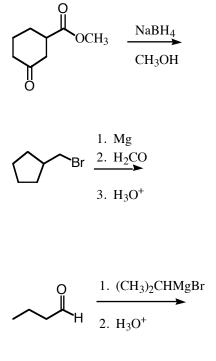
3. Circle the molecule with the highest boiling point. Put a square around the molecule with the highest water solubility. (4 points)

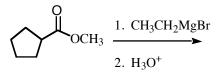


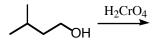
4. Rank the acidity of the following molecules, from 1 (strongest) to 4 (weakest). Explain <u>very</u> <u>briefly</u> why **A** and **B** have very different acidities.

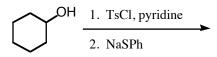


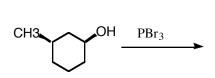
5. Draw the major products for the following reactions. (Assume excess quantities of reagents.) (3 points each, 21 points total)



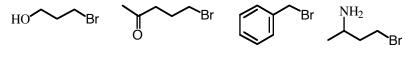




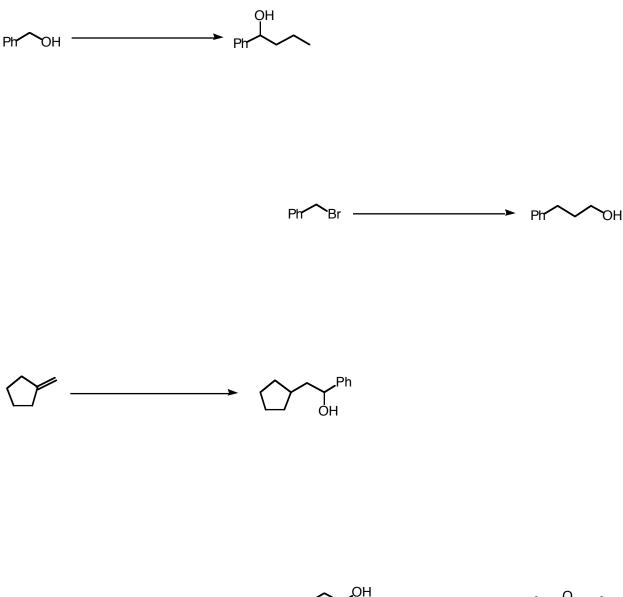




6. Which of the following would be suitable to use when forming a Grignard reagent? (3 points)



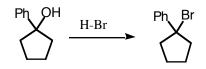
7. Provide the reagents necessary to accomplish the following transformations (5 each, 20 total)



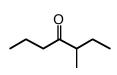


8. Draw a possible structure for an <u>achiral</u> molecule **A** with formula $C_5H_{12}O$, given that when H_2CrO_4 is added to **A** the solution turns green, and that the Lucas test with **A** takes about 3-4 minutes. (5 points)

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



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





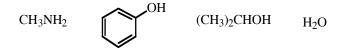
JASPERSE CHEM 360 TEST 1 VERSION 4 Reactions Involving Alcohols

1. Provide Names or Structures for the Following. (10 points total)

- a. (2R,5R)-cis-5-methyl-3-hepten-2-ol
- b. но Он

c. HO-CH₂CH₃

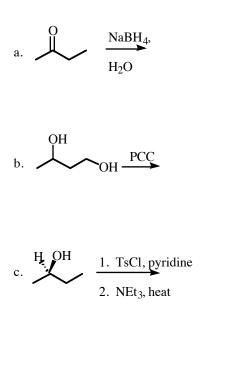
2. Rank the acidity of the following molecules, 1 being most and 4 being least acidic. (3 points)

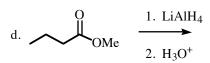


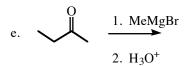
3. Complete the following acid-base reactions, and indicate whether the equilibrium favors the reactants or the products. (3 points each)

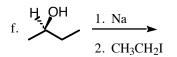
a.
$$\rightarrow$$
 + NaOH

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



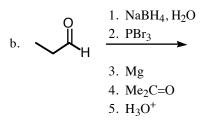




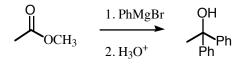


5. Draw the products for the following multistep syntheses. (5 points each)

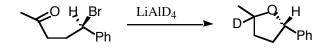
a.
$$()$$
 -OH $()$ -OH



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

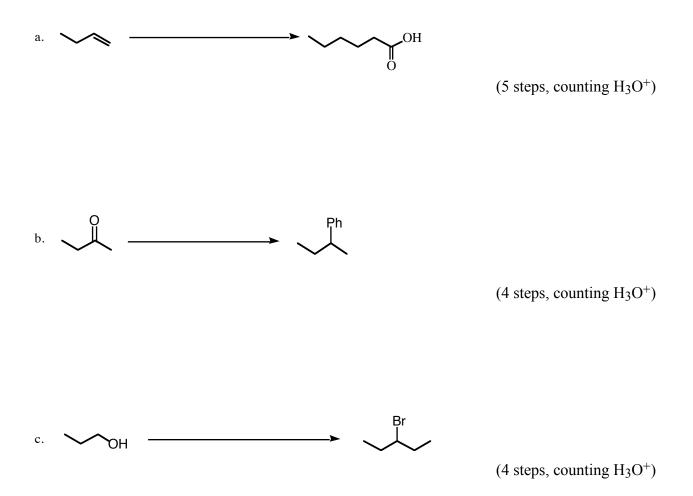


7. Draw the mechanism for the following reaction. Note: This is a slight twist on familiar stuff. The overall transformation appears unfamiliar, but the individual steps are actually familiar. (6 pts)



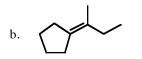
8. Suggest a structure for a compound "A" whose formula is $C_5H_{12}O$, that reacts instantly with the Lucas reagent (ZnCl₂/HCl), but does not cause an orange®green color change upon mixing with chromic acid. (4 points)

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)



10. Provide a synthesis for the following molecules. Permissible starting materials include alcohols or alkenes of ≤ 5 carbons, formaldehyde, ethylene oxide, 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.)

a.



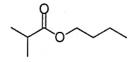
JASPERSE CHEM 360 TEST 2

VERSION 1

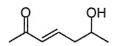


Ch. 12-13 NMR, IR

1. Predict the ¹H NMR spectrum. Include the approximate chemical shifts (1's, 2's, etc.), the integration, and the splitting (can use "s" for singlet; "d" for doublet; "t" for triplet "q" for quartet; and "m" for multiplet, anything more complex than a quartet). Note: for signals that are symmetry equivalent, do <u>not</u> list them twice.

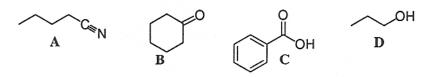


2. Predict the ¹³C NMR spectrum. Include the approximate chemical shifts (220-160, 160-100, 100-50, or 50-0) and the splitting if a couple carbon was taken (q, t, d, s).



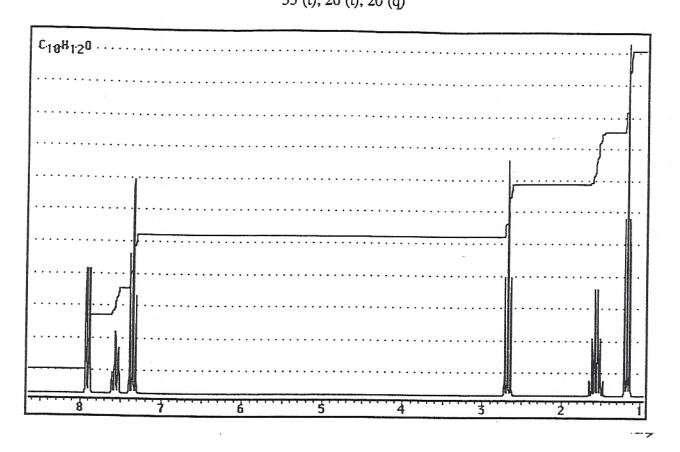
3. Match the following structures with the listed feature IR signals:

1) 3300-3200 2) 3300-2500, 1680 3) 2200 4) 1720



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 your work, make a structure guess, or tell me what you do know for sure.

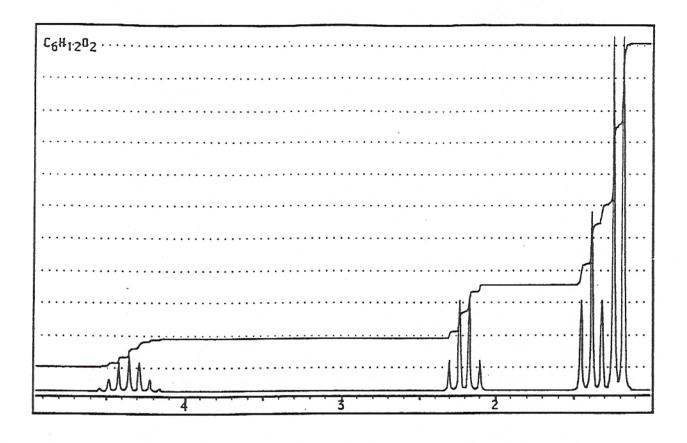
4. $C_{10}H_{12}O$ IR: 1670 ¹³C NMR: 210 (s, short), 150 (s, short), 130 (d, tall) 124 (d, tall), 120 (d), 33 (t), 26 (t), 20 (q)



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£.,

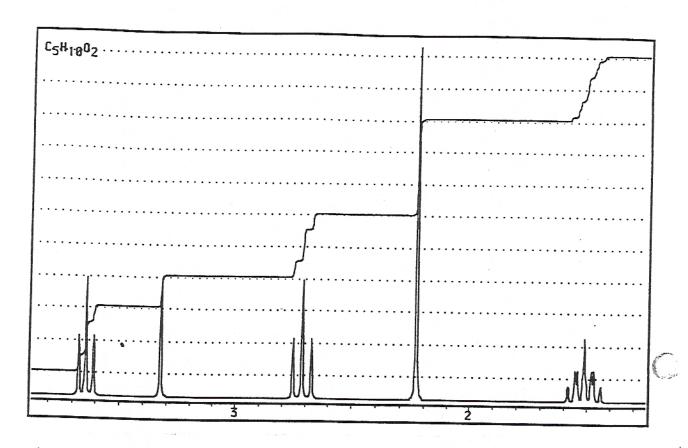
5. $C_6 H_{12}O_2$ IR: 1750 ¹³C NMR: 180 (s, short), 70 (d), 36 (t), 30 (q), 20 (q, extra tall)



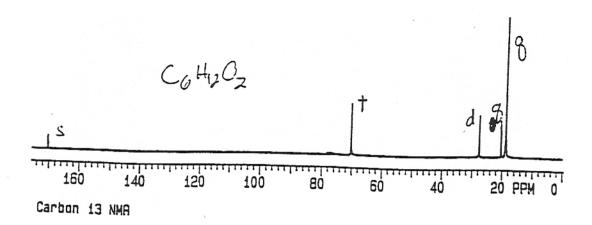
29

6. $C_5 H_{10}O_2$

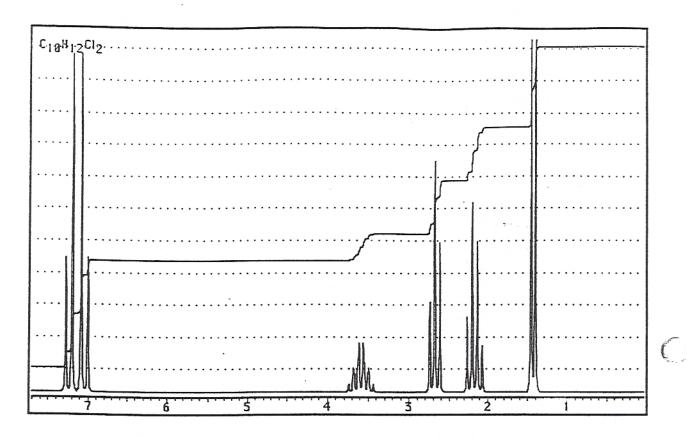
IR: 3300-3200, 1710 ¹³C NMR: 210 (s), 65 (t), 38 (t), 35 (t), 28 (q)



IR: 1745 (Note: There are two plausible solutions to this problem.)



8. $C_{10}H_{12}Cl_2$ ¹³C NMR 150 (s), 144 (s), 133 (d), 126 (d), 58 (d), 37 (t), 32 (t), 22 (q)



6

б

9. $C_6H_{14}O$

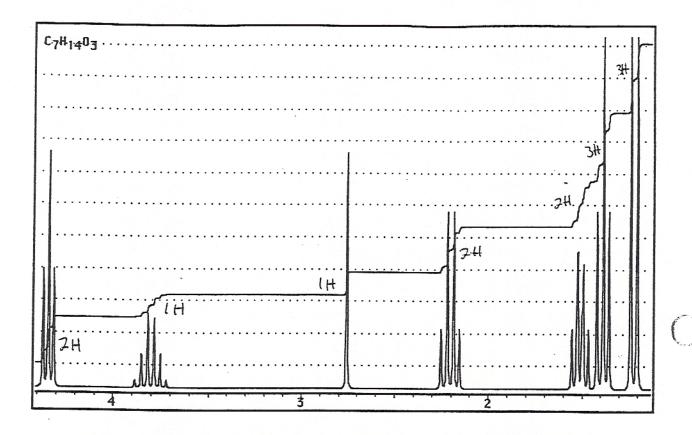
IR 3300-3200 ¹³C NMR 78 (d), 40 (d), 36 (t), 25 (q), 20 (q, extra tall)

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

(2 acceptable answers)

10. $C_7H_{14}O_3$

IR: 3300-3200, 1745 ¹³C NMR 180 (s), 75 (d), 65 (t), 38 (t), 30 (t), 25 (q), 20 (q)



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JASPERSE CHEM 360 TEST 2 Ch 12-13 NMR, IR

VERSION 2



1. Predict the ¹H NMR spectrum. Include approximate chemical shifts (1's, 2's, etc.), the integration, and the splitting (can use "s" for singlet; "d" for doublet; "t" for triplet; "q" for quartet, and "m" for multiplet, anything more complex than a quartet). Note: for signals that are symmetry equivalent, do <u>not</u> list them twice.

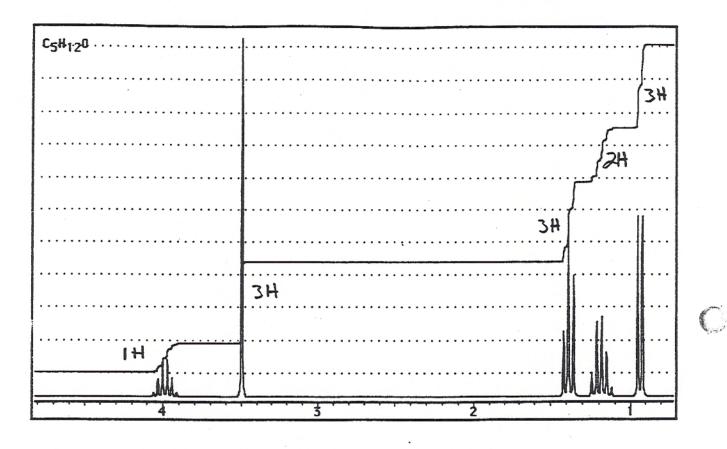
2. Predict the ¹³C NMR spectrum. Include the approximate chemical shifts (220-160, 160-100, 100-50, or 50-0) and the splitting (q, t, d, s).

3. Match the following structures with the listed feature IR signals.

А 1710 OH B 3300-3400 C 1680, 3300-2500

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 your work, make a structure, or tell me what you know for sure.

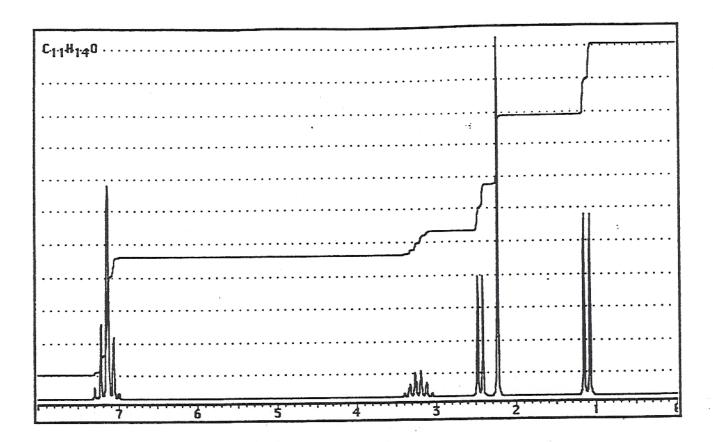
4. C₅H₁₂O IR: Nothing Interesting



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(<u>)</u> [

¹³C NMR: 202 (s), 152 (s), 134 (d), 127 (d), 122 (d), 42 (d), 35 (q), 20 (q)

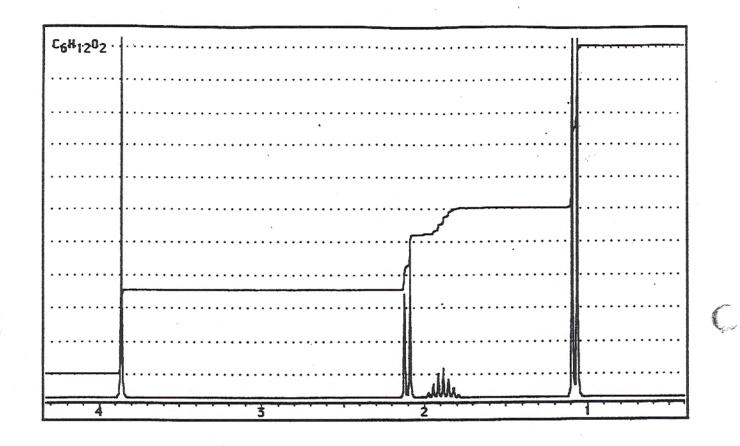


37

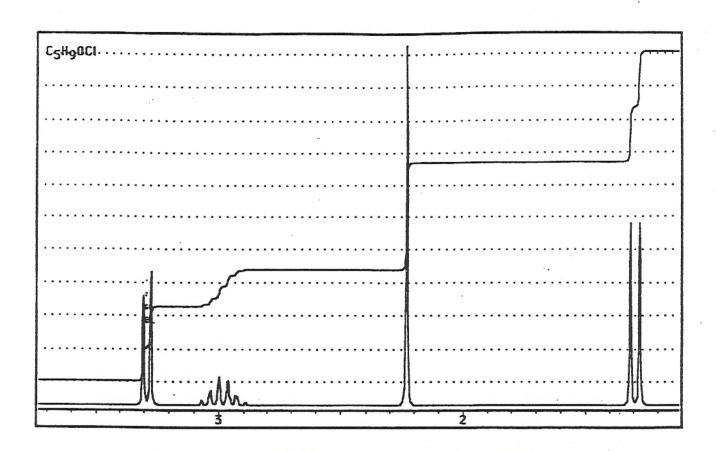
30(7)

6. C₆H₁₂O₂ IR: 1740

¹³C NMR: 175 (s), 65 (q), 42 (t), 37 (d), 18 (q)



7. C5H9OCl IR: 1710

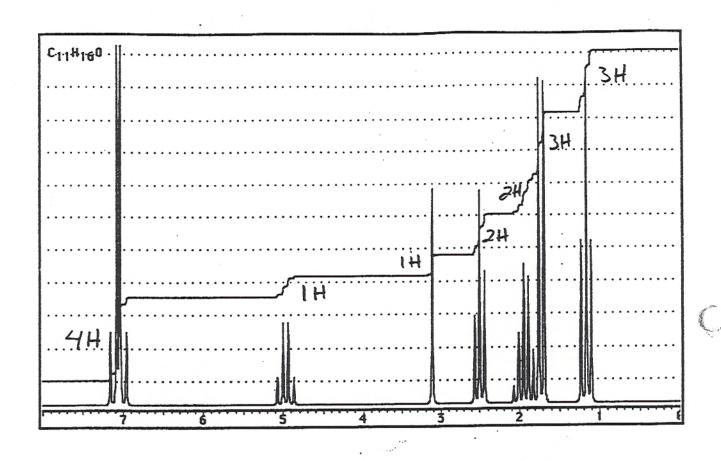


8. C₁₁H₁₆O IR: 3300-3200

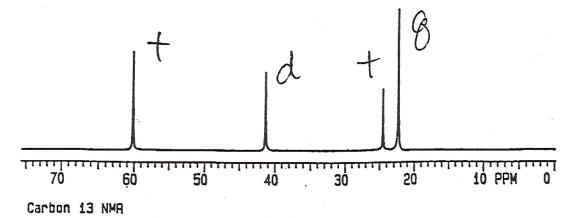
¹³C NMR: 148 (s), 144 (s), 133 (d), 124 (d), 80 (d), 42 (t), 35 (t), 30 (q), 20 (q)

40

6



9. C5H12O



41 ·

10. C₄H₇BrO₂ IR: 3300-2500, 1710

3H, t, 1.08 2H, multiplet, 1.89 1H, t, 4.23 1H, s (broad), 10.97 42 .

VERSION 3

Chein 360 Test 2

JASPERSE CHEM 360 TEST 2 Ch 12, 13 NMR, IR

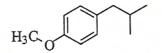
- 1. Predict the:
 - ¹H NMR spectrum [include approximate chemical shifts (1's, 2's, 3's, 4's, 5's, etc.), integration, and splitting]
 - ¹³C NMR spectrum [include approximate chemical shifts (0-50, 50-100, 100-150, or 150-220) and splitting]
 - identify any distinctive signals in the IR spectrum

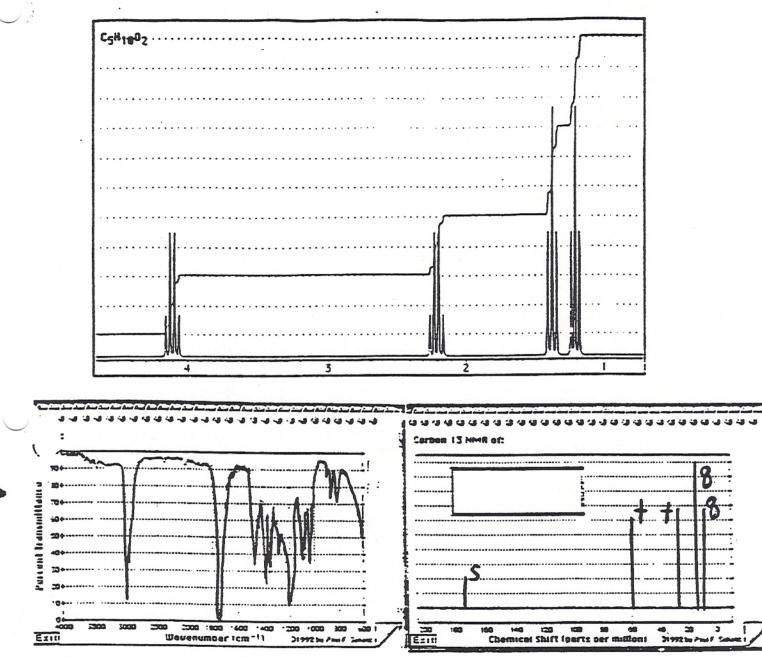
	¹ H NMR	¹³ C NMR	IR
Example: CH ₃ CH ₂ OCH ₃	1's 3H t 3's 2H q 3's 3H s	0-50, q 50-100, t 50-100, q	none
	¹ H NMR	¹³ C NMR	IR

- 2. For the following molecule,
 - Write how many "types" of H's there would be in the ¹H NMR spectrum (these are H's which might coincidentally overlap, but can't be assumed to be chemical shift equivalent)
 - Write how many different ¹³C NMR absorptions you would expect, and
 - Write what the ¹³C NMR splitting would be, i.e. singlet, doublet, triplet, or quartet for the ¹³C NMR absorptions.

Number of	Number of ¹³ C	Expected
Nonequivalent	Absorptions	Splittings
<u>H's in H-NMR</u>	in ¹³ C NMR	in ¹³ C NMR
3	4	q, t, s, q
Number of	Number of ¹³ C	Expected
Nonequivalent	Absorptions	Splittings
<u>H's in H-NMR</u>	in ¹³ C NMR	in ¹³ C NMR

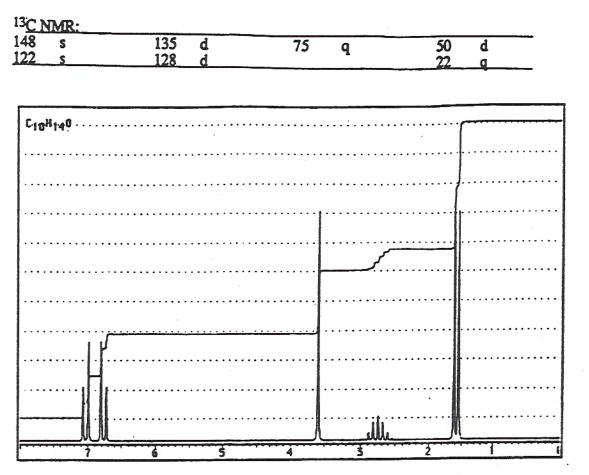
Example:





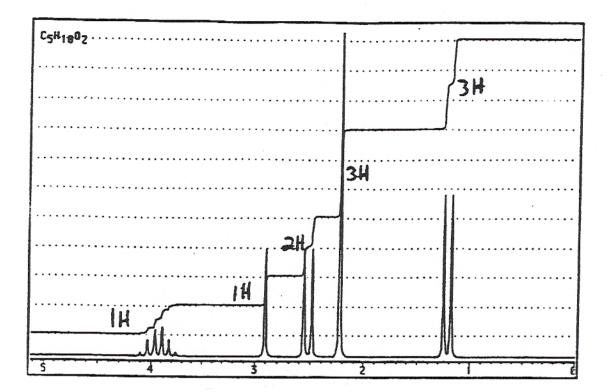
Provide Structures Based on the Following Spectroscopic Data (8 points each) 4. $C_5H_{10}O_2$

5. C₁₀H₁₄O



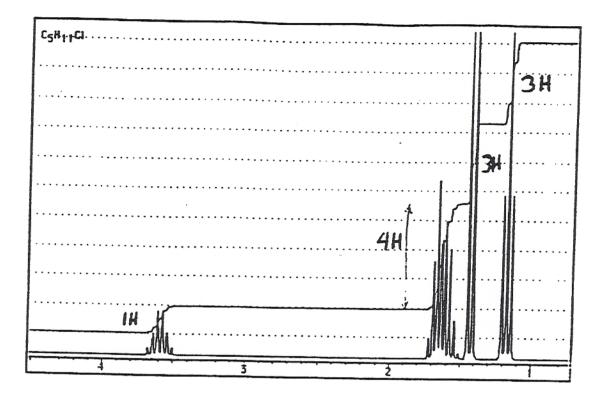
6. C5H10O2

IR: 1710 (strong), 3300-3500 (broad, strong)

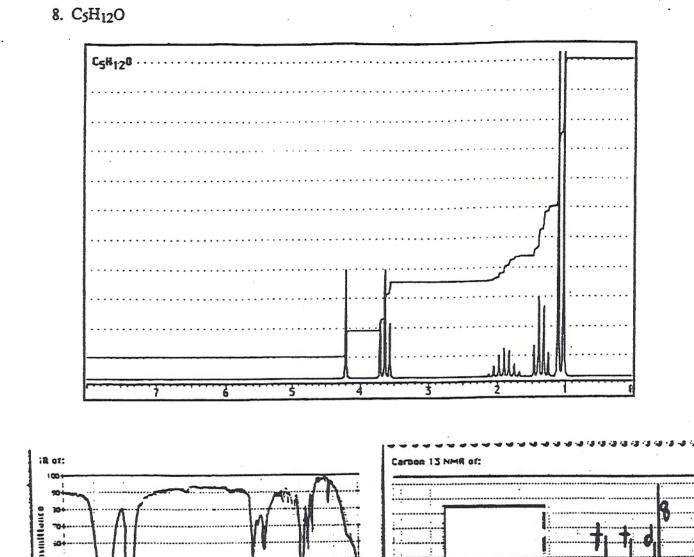


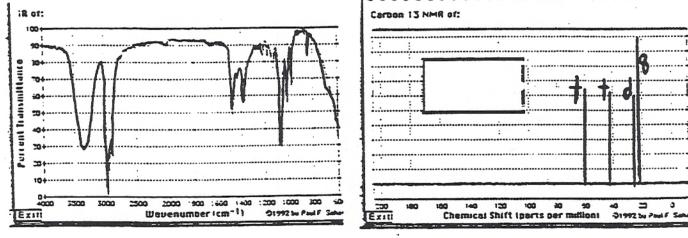
7. C₅H₁₁Cl

¹³C NMR: 60 (d), 40 (t), 37 (t), 33 (q), 20 (q)



47





9. C₄H₈O₂ triplet, 1.02, 3H sextet, 1.43, 2H triplet, 2.35, 2H singlet, 10.95, 1H

IR 1715 cm⁻¹ and broad 2500-3000

JASPERSE CHEM 360 TEST 2 Ch 12, 13 NMR, IR

VERSION 4

NOTE: This Version is Longer than the Real Test Will Be

- Jaspfsike Chem360 Test2 Vevsion4
- 1. Predict the ¹H NMR spectra for the following molecules. Include predicted:
 - chemical shifts
 - integration
 - splitting pattern (singlet, doublet, triplet, quartet, etc., multiplet)

Example

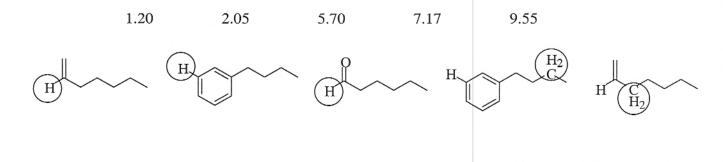
CI Br

3's, 2H, t 1's (or 2's), 2H, pentet (or multiplet) 3's, 2H, t

~~ a.

b.

- 2. Assign the dimethylbenzene isomer for which the ¹³C NMR spectrum has:
 - a. 3 signals (q, s, d)
 - b. 4 signals (q, s, d, d)
 - c. 5 signals (q, s, d, d, d)
- 3. Match the circled proton or protons in the following compounds with the correct chemical shift.

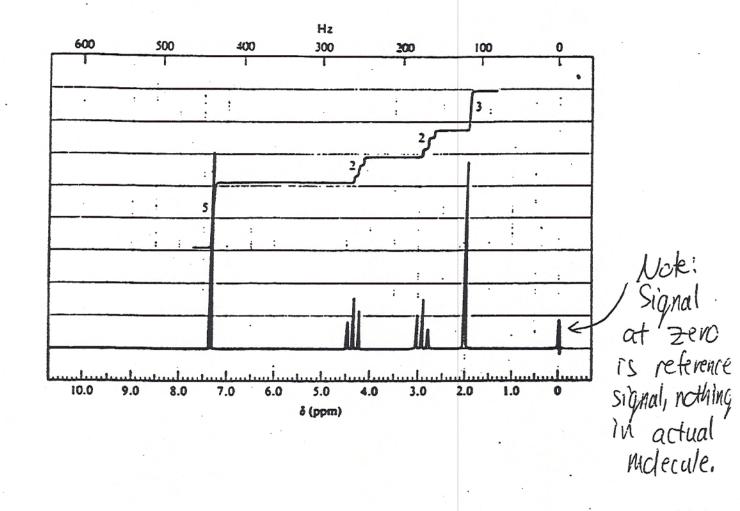


DRAW STRUCTURES FOR THE MOLECULES IN PROBLEMS 3-9

C10H12O2

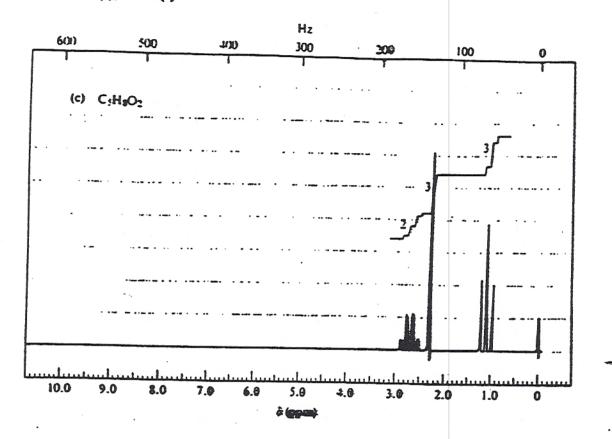
IK: 1740 (strong), 750 (strong), 700 (strong)

¹³C NMR: 185 (s), 155 (s), 135 (d), 130 (d), 128 (d), 35 (t), 28 (t), 20 (q)



65

C5H8O2 IR: 1720 (s), 1725 (s)

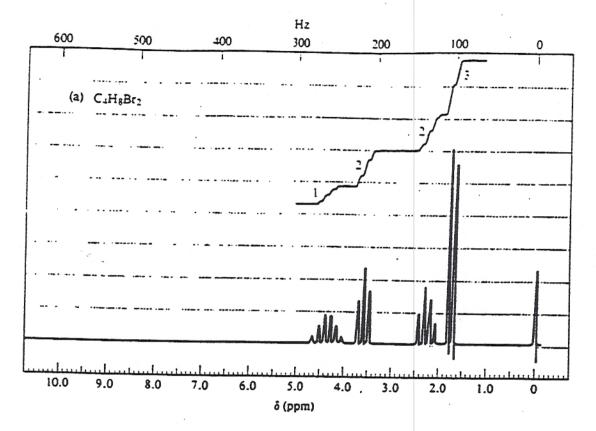


· 53

$(5. C_{4}H_{8}Br_{2})$

IR: nothing interesting

¹³C NMR: 45 (d), 37 (t), 24 (t), 18 (q)



(G) C11H16O

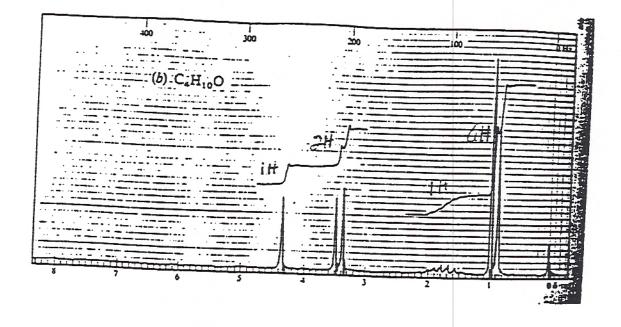
IR: 820 (strong)

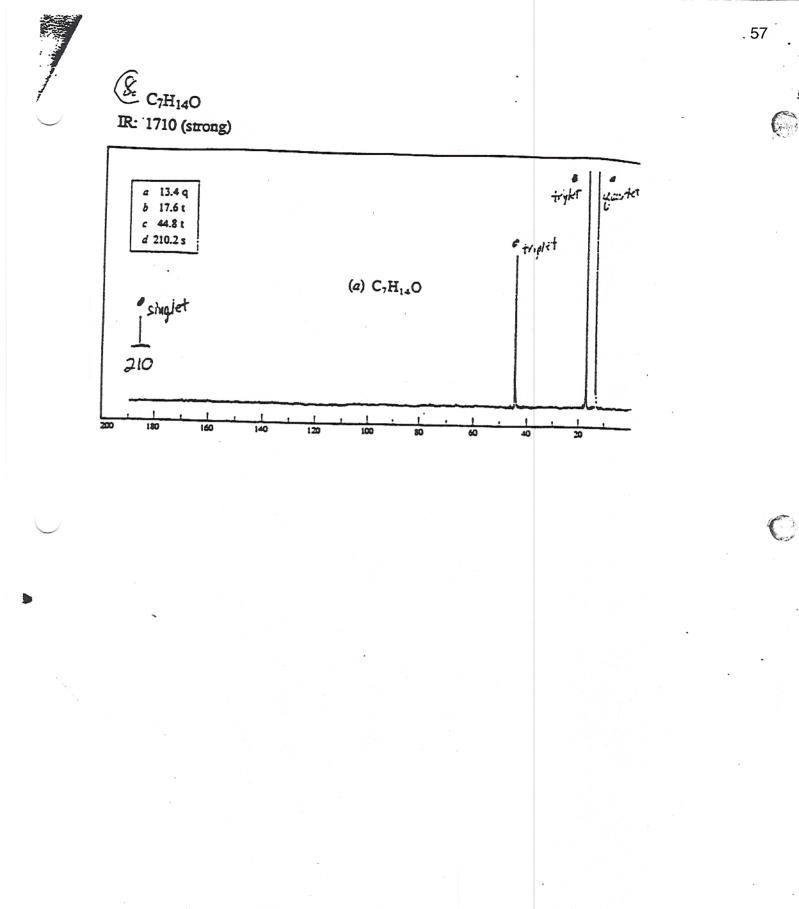
¹³C: 145 (s), 132 (s), 128 (d), 120 (d), 75 (t), 35 (d), 20 (q), 18 (q) ¹H NMR: 1.25 (6H, d), 1.30 (3H, t), 2.90 (m, 1H), 4.15 (2H, q), 6.66 (2H, d), \leq 6.97 (2H, d)

55

- 5

, C₄H10O





8

C

ż,

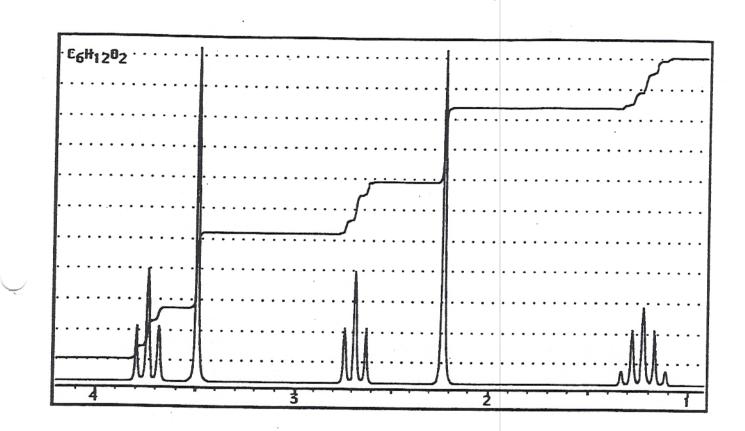
15. Show the structures for the following molecule, based on the spectroscopic information provided. (10 points)

C6H12O2

٩.,

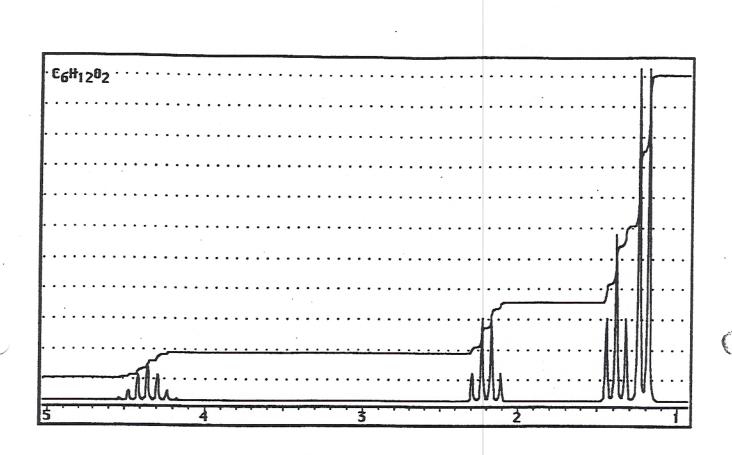
IR: 1710, strong

¹³C NMR: 200 (s), 75 (t), 65 (q), 40 (t), 30 (t), 20 (q)



(10),

DS. Show the structures for the following molecule, based on the spectroscopic information provided. (10 points)

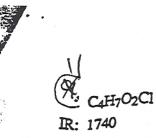


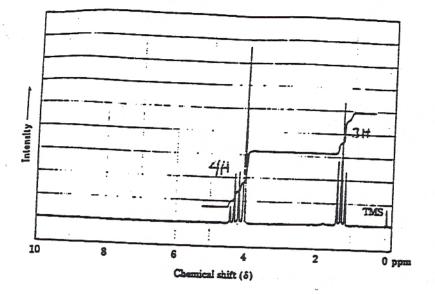
C₆H₁₂O₂ IR: 1745, strong 1

¹³C NMR: 20 (q), 30 (q), 48 (t), 78 (d), 185 (s)

. <u>`</u>59

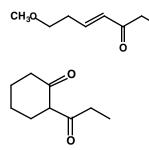
()



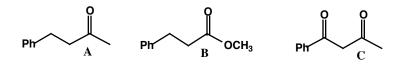


JASPERSECHEM 360TEST 3VERSION 1Ch 18Ketones and AldehydesCh 22Additions and Conensations of Enols and Enolate Ions

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

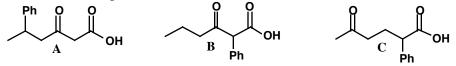


- 2. Of the following structures,
- a. Which will be "completely" (>98%) deprotonated by LDA (LiN-iPr₂)? (2 points)
- b. Which will be "completely" (>98%) deprotonated by NaOH? (2 points)

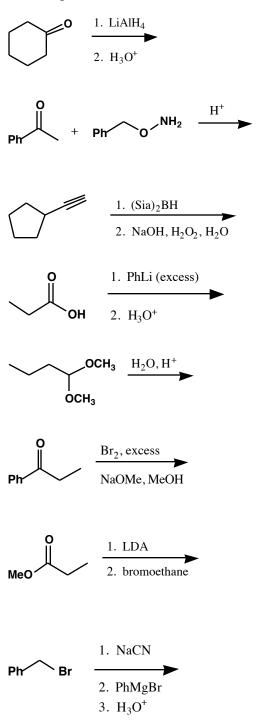


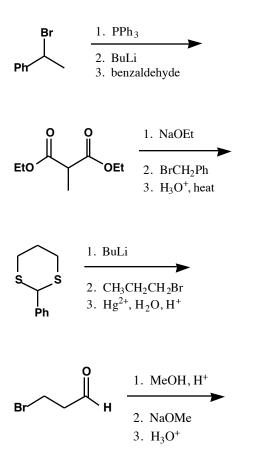
3. An unknown **X** has formula C_4H_8O . It gives 1) an orange precipitate upon treatment with 2,4dinitrophenylhydrazine (2,4-DNP) and it gives 2) a silver mirror upon treatment with Tollen's reagent [Ag(NH₃)₂⁺OH⁻]. 3) It does not react with Br₂ in dichloromethane solvent. 4) Included in the ¹H NMR (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)

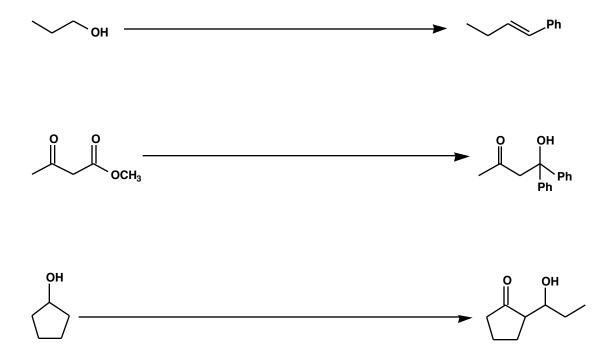


5. Synthesis Reactions. Draw the feature product of the following reactions (need not show any byproducts). NOTE: In every case, the product should be a stable, isolable **product**; an "intermediate" structure will not receive full credit. (2 or 3 points each; 1st 7 worth 2 points; last 5 worth 3 points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

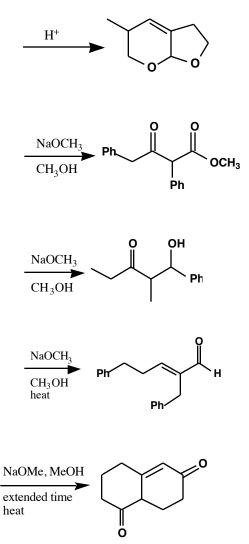




6. Provide Reagents for the Following Transformations: (4 points each)

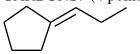


7. Put in the starting materials from which the following structures would be produced. Depending on the product, the appropriate starting material may be either a single molecule, two of the same molecule, or two different molecules. For the last problem, you are required to start from two separate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

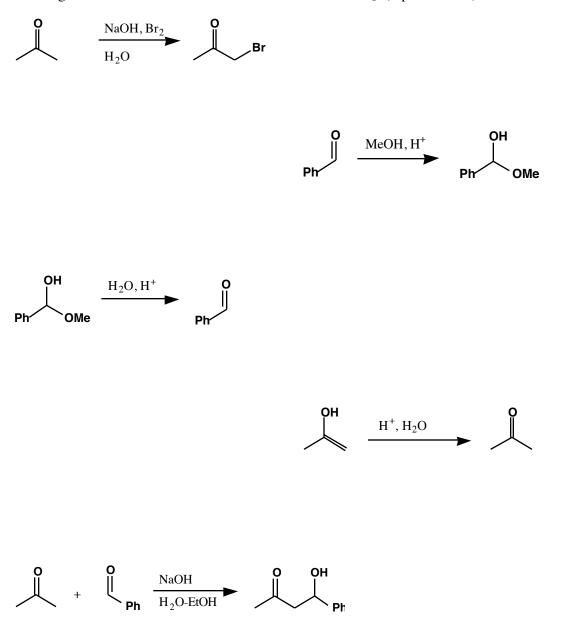


Note: The Starting Materials are two Separate Molecules

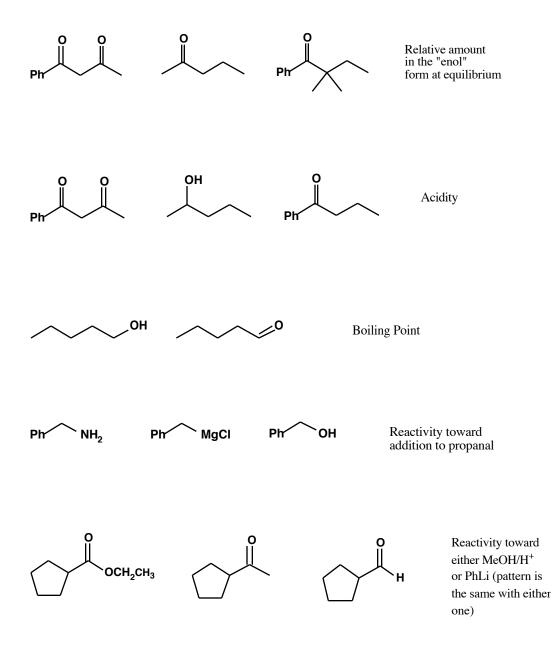
8. Design a synthesis for the following alkene, FROM ALCOHOLS WITH NO MORE THAN 5 CARBONS. (4 points)



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)

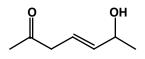


10. Rank the following, with 1 being highest, or most. (2 points each)



JASPERSECHEM 360TEST 3VERSION 2Ch 18Ketones and AldehydesCh 22Additions 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)

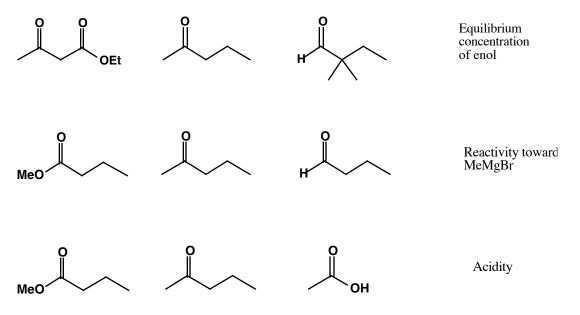


3-isopropylbenzaldehyde

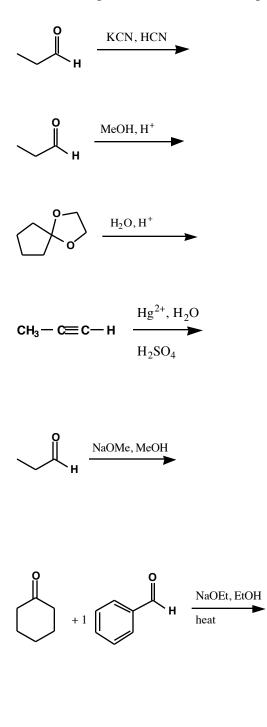
Ph H

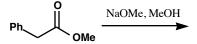
optically active

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

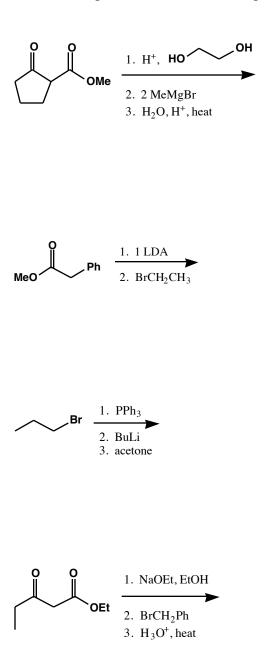


3. Draw the products for the following reactions (3 pt each)

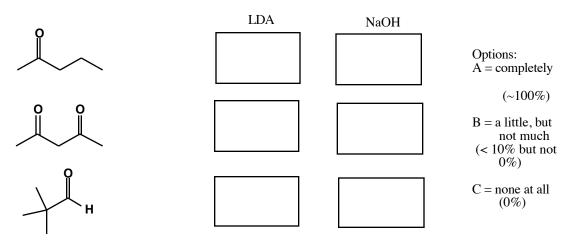




4. Draw the products for the following multistep reactions. (3 pt each)

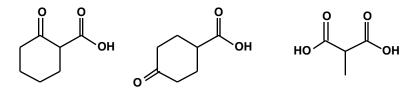


5. For the following chemicals, describe the extent to which each would be deprotonated by LDA (LiN-iPr₂) or by NaOH at equilibrium. Fill in all 6 boxes. Options are complete deprotonation (A), a little deprotonation (B), and no deprotonation (C). (6 pt)

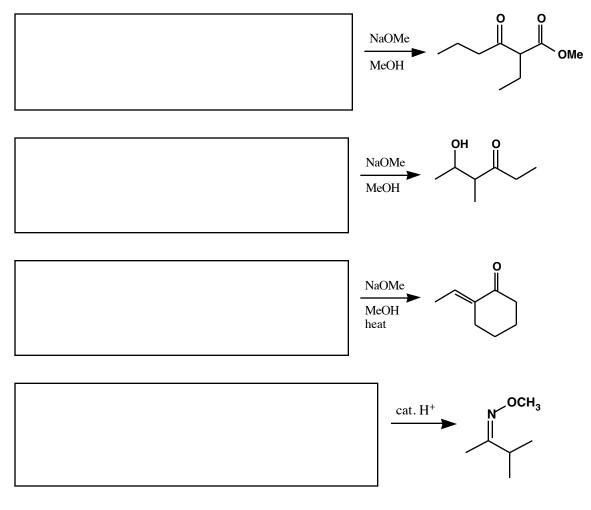


- 6. Suggest a plausible structure consistent with the following information. (5 pt)
- a. It reacts positively with 2,4-dinitrophenylhydrazine.
- b. It reacts positively with NaOH/I₂, the iodoform test
- c. It does not react with Tollen's reagent [Ag(NH₃)₂+OH⁻].
- d. It does not react with Br_2 in dichloromethane solvent.
- e. Chemical formula is C7H12O
- f. It's ¹³C spectrum shows 5 carbons (1 singlet, 1 doublet, 2 triplets, and 1 quartet)

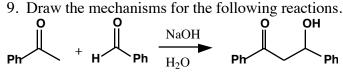
7. Which of the following would not undergo decarboxylation (loss of CO₂) upon heating? (2 pt)



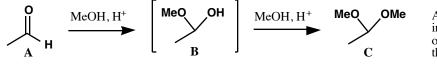
8. Put in the starting materials from which the following would be made. (3 each)



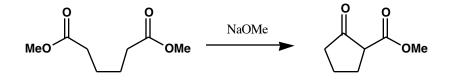
9. Draw the mechanisms for the following reactions. (4 pt each)

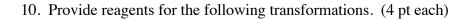


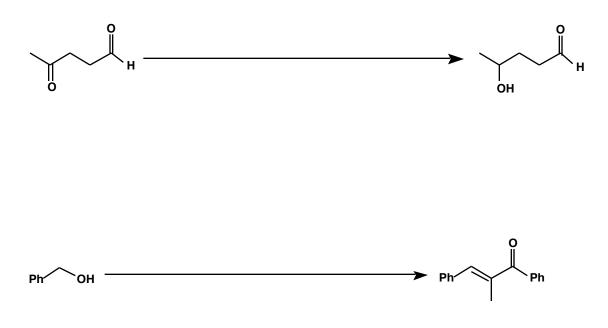
(Note: this one counts as 2 problems, 8 points total)



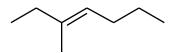
All steps are actually in equilibrium, but I only want you to show the forward direction







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



JASPERSE CHEM 360 TEST 3

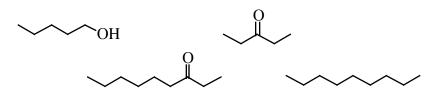
VERSION 3

Ch 18 Ketones and Aldehydes

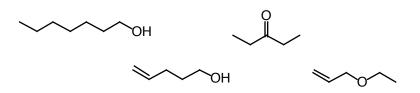
Ch 22 Additions and Conensations of Enols and Enolate Ions

1. Physical Properties.

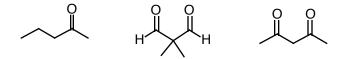
a. Rank the following according to <u>solubility in water</u>, 1 being most soluble, 4 being least soluble.



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.



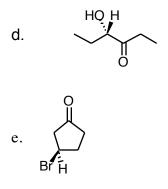
d. Rank the following according to <u>acidity</u>, 1 being most acidic and 4 least acidic.

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

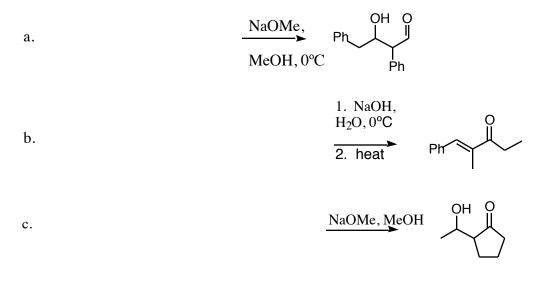
a. 3-propylbenzaldehyde

b. (S)-3-phenylbutanal

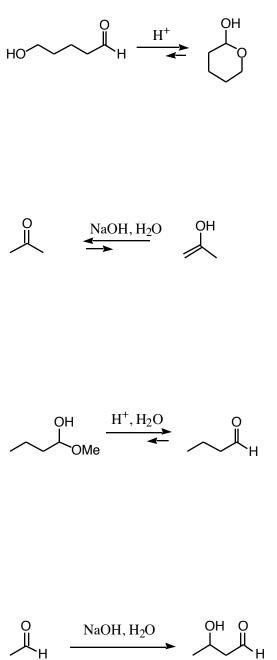
c. (Z)-2-methyl-4-hepten-3-one



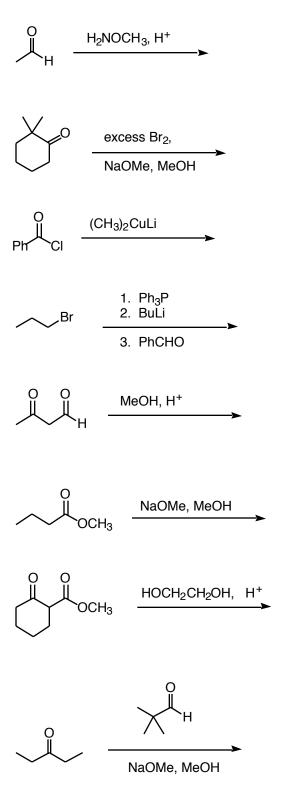
3. Identify the starting carbonyl compound or compounds from which the following aldol-type reaction products are formed. (12 points)

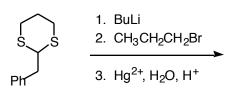


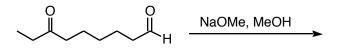
4. Draw the mechanisms for the following transformations.



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





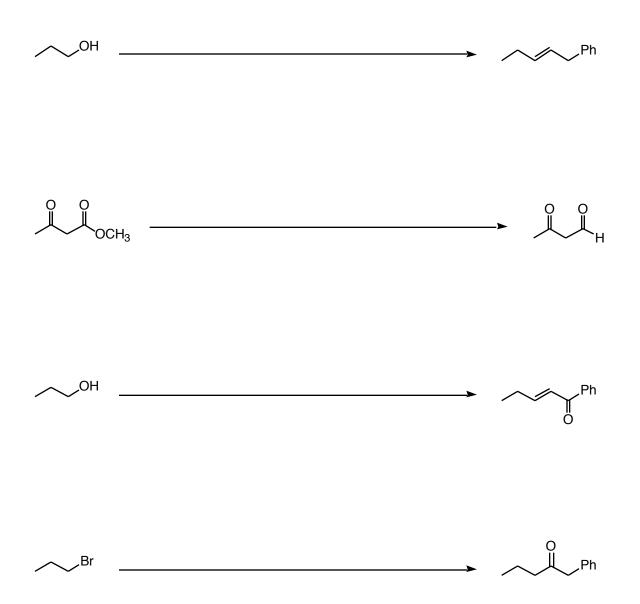


PhCHO, NaOMe, MeOH

$$\begin{array}{c} OH \\ \hline \\ 2. \ Ph_3P=CHPh \end{array}$$

NaOMe, MeOH, heat

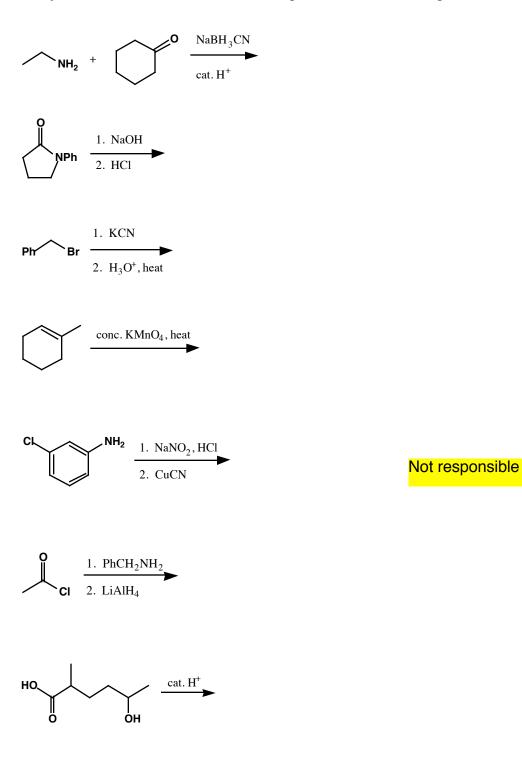
80

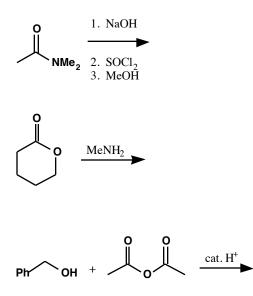


JASPERSE	CHEM 360	TEST 4	VERSION 1
Ch 19 Amines			
Ch 20 Carboxylic	e Acids		

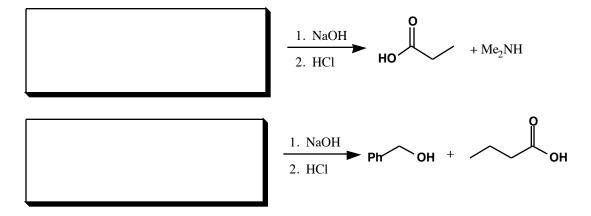
Ch 21 Carboxylic Acid Derivatieves

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



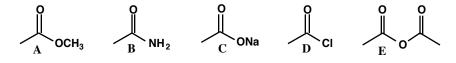


2. Draw the starting materials for the following hydrolysis reactions. (2 pts each)



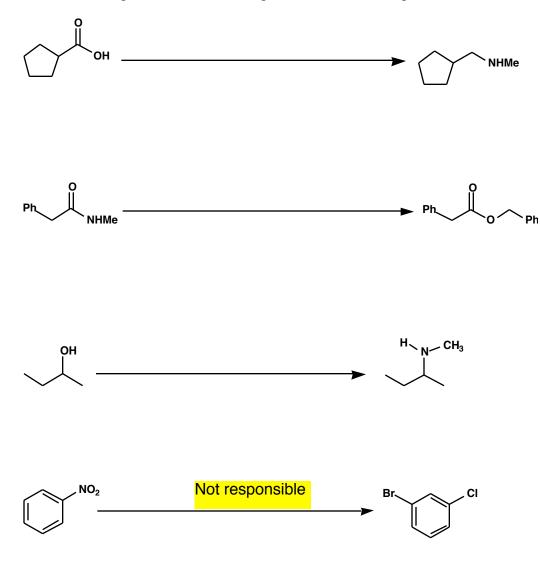
3. a) Which one(s) of the following will react spontaneously with H_2O ? (2 pts)

b) Which one(s) will react spontaneously with Me_2NH ? (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)



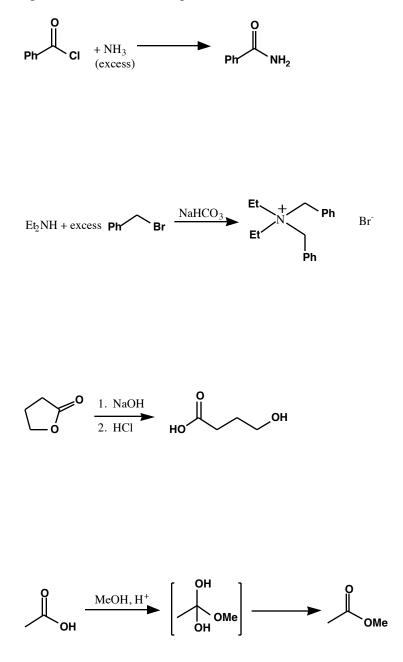


5. Provide Reagents for the Following Transformations (4 pts each)

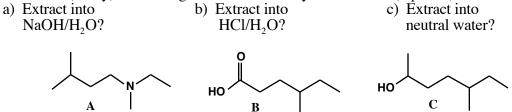
6. Name the Following or Draw the Structure (2 pts each)

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

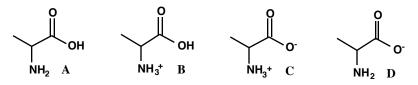
7. Provide Mechanisms for the Following Reactions. (Note: In some cases, these may be "partial" reactions.) (16 points)



8. Which (if any) after being dissolved in diethyl ether, will: (4 points)



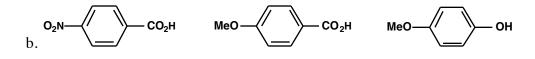
9. Of the following, which form would exist at: (4 points)
a) pH = 2 (acidic)
b) pH = 7 (neutral)
c) pH = 12 (basic)



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

11. Rank the acidity of the following, 1 being most acidic, 3 being least (2 pts each)

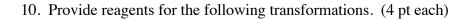
a. ethanoic acid $CH_3NH_3^+Cl^-$ ethanol

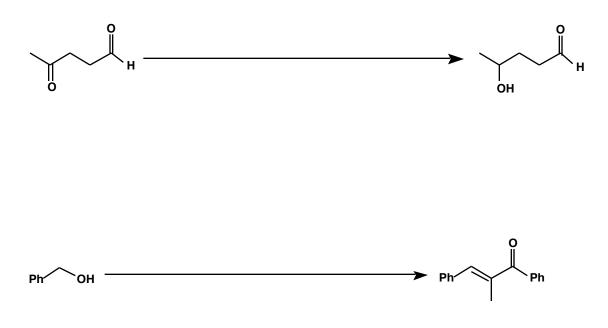


- 12. Rank the following in order of increasing basicity (2 points each)
- a. NH_3 CH_3NH_2 $PhNH_2$
- b. NaOH CH_3NH_2 sodium ethanoate

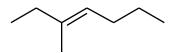
c.

NН



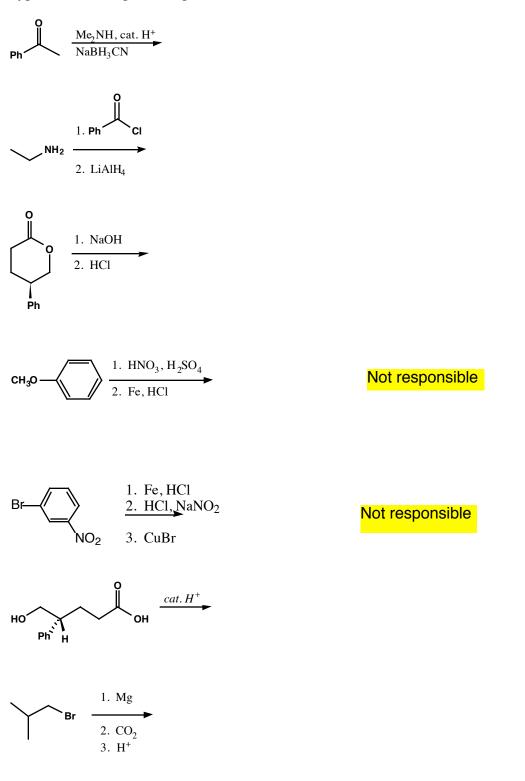


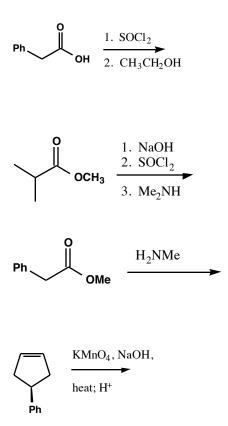
11. Design a synthesis for the following alkene **FROM ALCOHOLS WITH NO MORE THAN 5 CARBONS**. (6 pt)



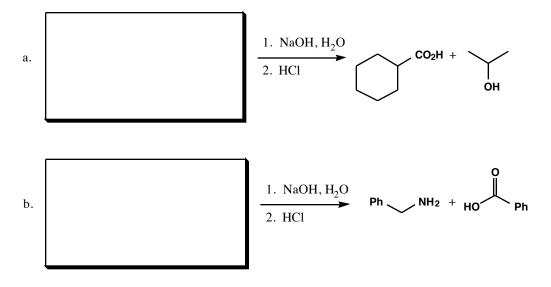
JASPERSECHEM 360TEST 4VERSION 2Ch 19-21 Amines, Carboxylic Acids, Carboxylic Acid Derivatives

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

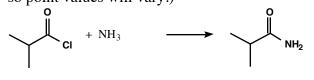




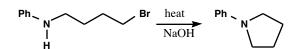
2. Hydrolysis Reactions. Draw the starting materials for the following hydrolysis reactions. (4 points)

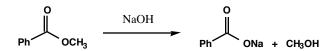


3. Draw the <u>Mechanisms</u> for the following reactions. (16 points total. Some are relatively trivial, so point values will vary.)

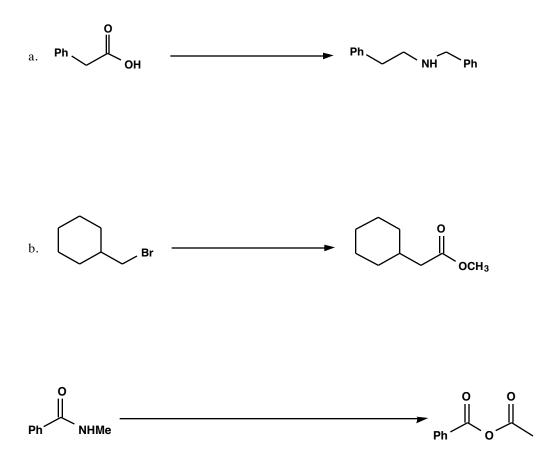


$$\underbrace{\overset{\mathsf{O}}{\underset{\mathsf{OMe}}{\overset{\mathrm{H}_{2}\mathrm{O},\,\mathrm{H}^{+}}{\longrightarrow}}}}_{\mathsf{OMe}} \left[\underbrace{\overset{\mathsf{OH}}{\underset{\mathsf{OMe}}{\overset{\mathsf{OH}}{\longrightarrow}}}}_{\mathsf{OH}} \right] \xrightarrow{\mathsf{O}}_{\mathsf{OH}}$$



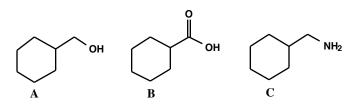


4. Provide Reagents for the following Transformations (12 points)



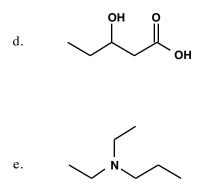
5. Which (if any) after being dissolved in diethyl ether, will: (6 points. Note: The answers may be none or more than one, you tell me!)

- a) Extract into NaOH/H₂O?
- b) Extract into HCl/H₂O?
- c) Extract into water?

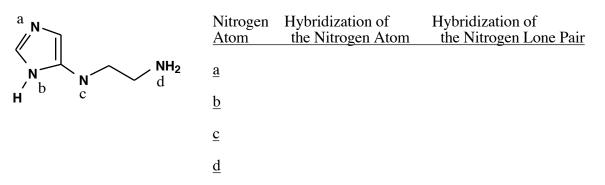


6. Nomenclature. Provide Either the Name or the Structure for the Following Chemicals. (8 points)

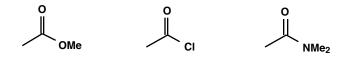
- a. N-propyl-5-methyl-1-hexanamine
- b. (R)-2-bromopropanoic acid



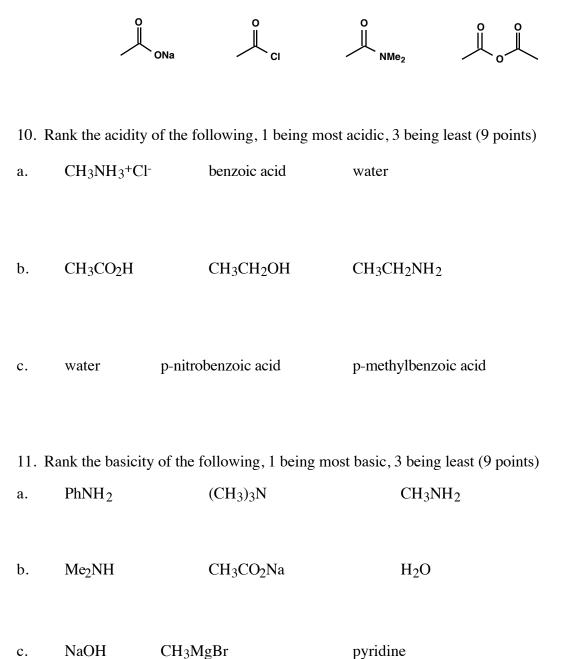
7. For each nitrogen a-d, identify the hybridization of the <u>nitrogen atom</u>, and identify the hybridization of the <u>nitrogen lone pair</u>. (6 points, 2 points off for 1st error, 1 for each additional)



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



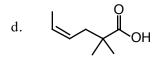
9. Circle the compounds, if any, (may be none, one, or more than one) that would <u>not</u> react with methanol to give a methyl ester: (4 points)

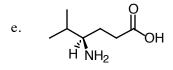


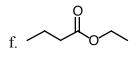
JASPERSECHEM 360TEST 4VERSION 3Ch 19-21 Amines, Carboxylic Acids, Carboxylic Acid Derivatives

1. Nomenclature. Provide Either the Name or the Structure for the Following Chemicals. (10 points)

- a. N-ethyl-N-methyl-4-methyl-1-pentanamine
- b. sodium (R)-3-hydroxybutanoate
- c. 4-methylpentanoyl chloride







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).]

H _e N f	Nitrogen <u>Atom</u>	Hybridization of the Nitrogen Atom	Hybridization of the Nitrogen Lone Pair
^a N M d	<u>a</u>		
	<u>b</u>		
	<u>c</u>		
	<u>d</u>		
	<u>e</u>		
	<u>f</u>		

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

a.
$$Ph \longrightarrow Br \xrightarrow{1. Mg}_{2. CO_{2}}$$

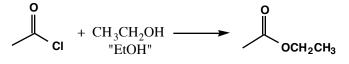
$$H^{+}$$
b.
$$Ph \longrightarrow NMe_{2} \xrightarrow{2. SOCl_{2}}_{3. PhCH_{2}OH}$$
b.
$$Ph \xrightarrow{0}_{1. LiAIH_{4}} \xrightarrow{1. SOCl_{2}}_{3. PhCH_{2}OH}$$
c.
$$O \xrightarrow{1. LiAIH_{4}}_{2. H_{3}O^{+}}$$
d.
$$O \xrightarrow{0}_{1. LiAIH_{4}} \xrightarrow{1. SOCl_{2}}_{3. LiAIH_{4}; H_{2}O}$$
e.
$$O \xrightarrow{0}_{1. LiAIH_{4}; H_{2}O} \xrightarrow{1. IAIH_{4}; H_{2}O}$$
f.
$$O \xrightarrow{0}_{1. IAIH_{4}; H_{2}O} \xrightarrow{1. NaOH, H_{2}O}_{2. H^{+}}$$

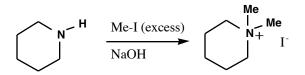
4. Synthesis Reactions. Draw the feature product of the following reactions (need not show any byproducts). (15 points)

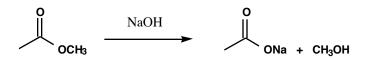
a.
$$HO \longrightarrow HO \longrightarrow HO \longrightarrow HOH \oplus HOh$$

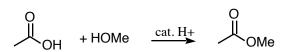
e.
$$(1. \text{ KMnO}_4)$$
2. excess MeLi
3. H₃O⁺

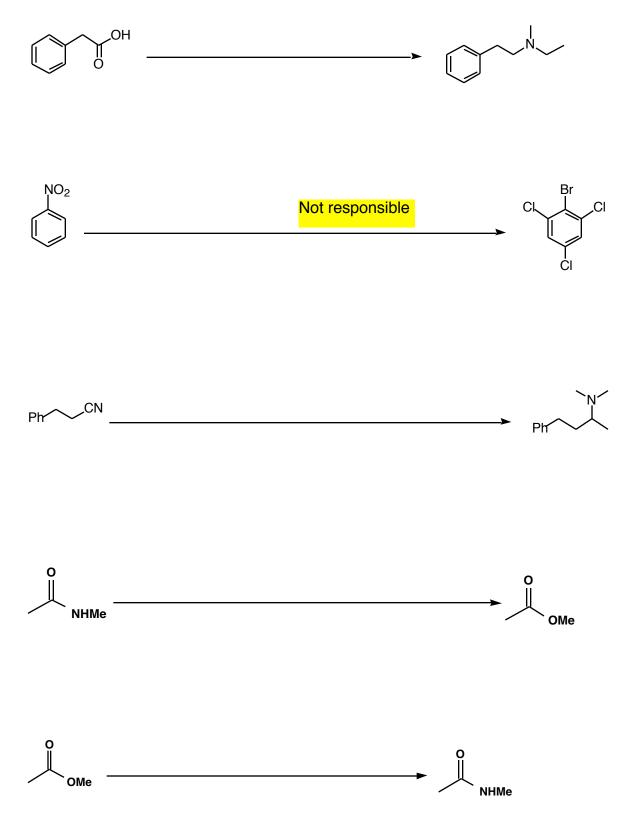
5. Draw the mechanisms for the following reactions. (5 points)



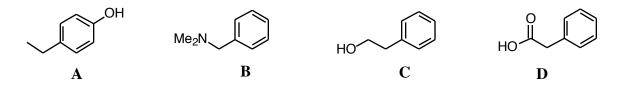




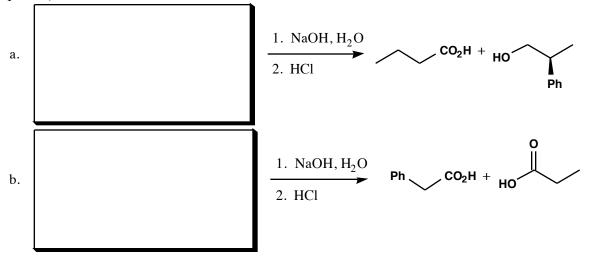




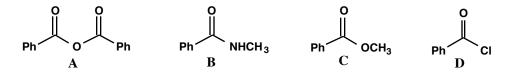
- a) Extract into NaOH/H₂O?
- b) Extract into HCl/H₂O?
- c) Extract into water?



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)

 $\mathbf{A} + \mathbf{H}_2 \mathbf{N} \mathbf{C} \mathbf{H}_3 \Rightarrow \mathbf{B}$ $\mathbf{A} + \mathbf{H} \mathbf{O} \mathbf{C} \mathbf{H}_3 \Rightarrow \mathbf{C}$ $\mathbf{A} + \mathbf{H} \mathbf{C} \mathbf{I} \Rightarrow \mathbf{D}$

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

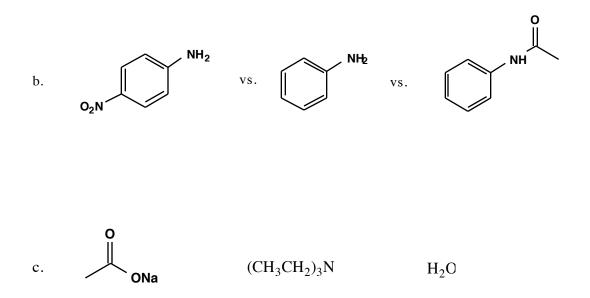
a. acetic acid vs. water vs. NH4⁺Cl⁻

b. CH₃OH vs. CH₃NH₂ vs. F₂CHOH

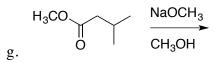
c. p-methoxybenzoic acid vs. benzoic acid vs. acetone

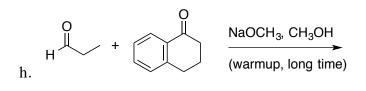
11. Rank the basicity of the following, 1 being most basic, 3 being least (3 points each)

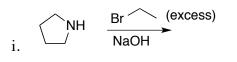
a. CH₃OH vs. PhNH₂ vs. CH₃NH₂

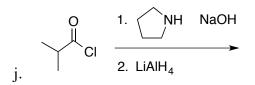


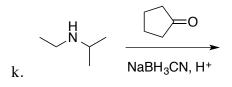
1. Give the major product for the following reactions. (3 points each)

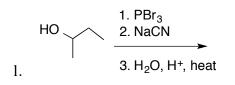


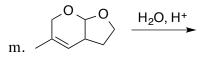


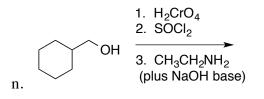




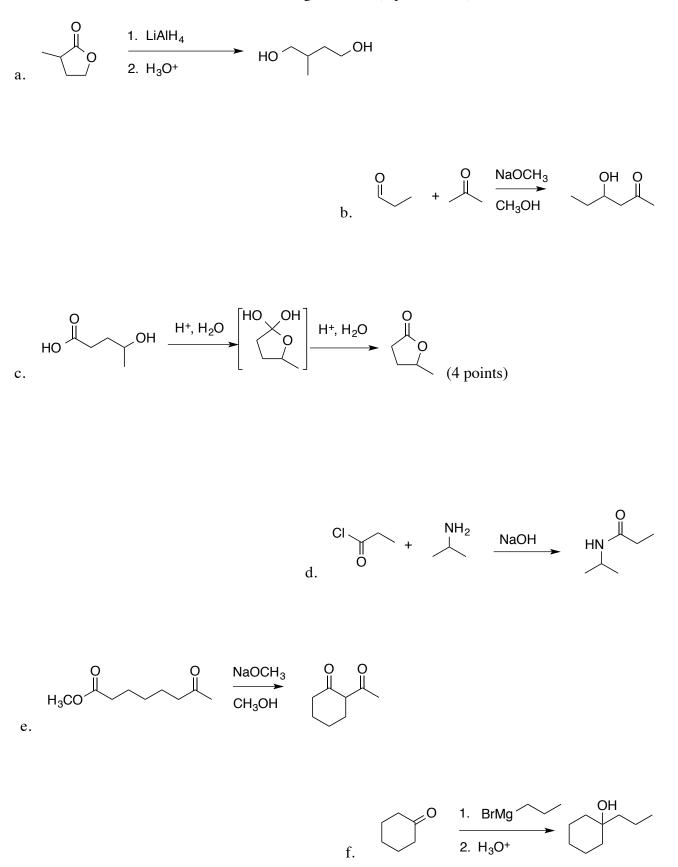




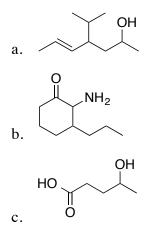




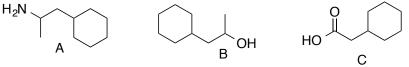
2. Provide the mechanisms for the following reactons (3 points each)



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



4. Separatory Funnel/Extraction: 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.).



No reaction

Reacts, makes 2nd layer.

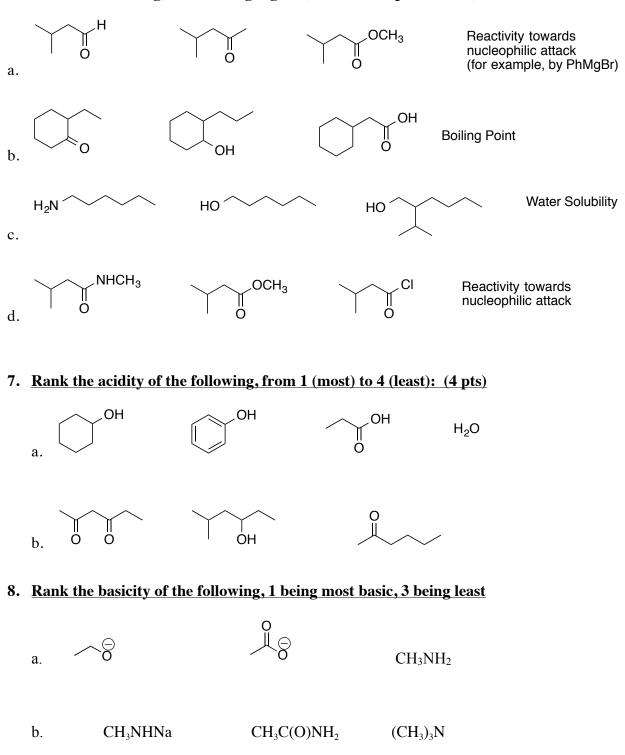
Reacts, turns green/brown, precipitate forms.

- a. Identify which (if any) would **extract out into the aqueous layer** if treated with **basic** water (NaOH/H₂O).
- b. Identify which (if any) would extract out into the aqueous layer if treated with acid water (HCl/H₂O).
- c. Identify which (if any) would extract out into the aqueous layer if treated with neutral distilled water (H₂O).
- 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 ٠ $C_6H_{12}O_2$
 - Hydrogenation Test H₂/Pt •

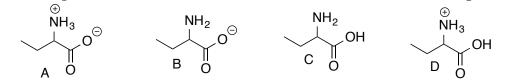
٠

- Chromic Acid Test H₂CrO₄ •
- Lucas Test HCl/ZnCl₂ •
- Reacts, yellow precipitate 2,4-DNP Test 2,4-dinitrophenylhydrazine •
- $Ag(NH_3)_2^+OH^-$ **Tollens** Test • Iodoform Test
 - No reaction 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) •

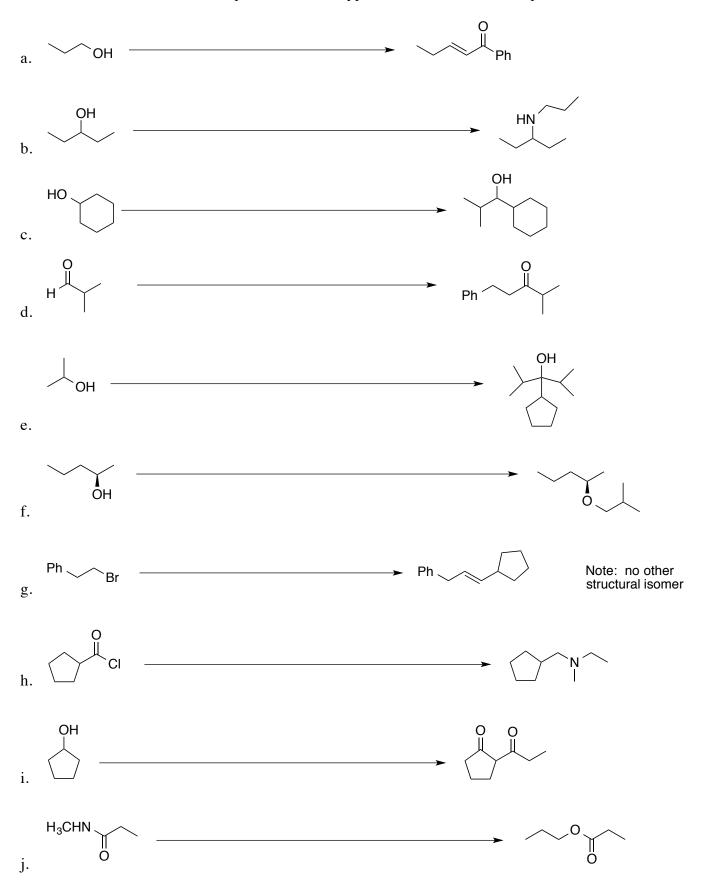
6. Rank the following, with 1 being highest, or most. (2 points each)



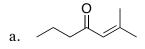
9. Of the following, which one form would exist under basic conditions? (ex, pH = 10)

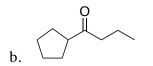


- 10. Provide the reagents necessary to accomplish the following transformations (4 points each). You may use anything you wish, as big as you like.
 - Note 1: Real test will have 6 problems of this type, but I included more for practice



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)

1. NaOH, H₂O HO 2. HCl + H₂N _

a.

b.

 \int_{0} 1. LiAlH₄ OH Note: Starting Material includes a ring, and has the formula $C_7H_{12}O_2$ OH 2. H₃O+ NaOCH₃ CH₃OH heat H+ റ

d.

c.

13. 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. (5 pts)

	Source	Chem Shift	Integration	<u>Splitting</u>
$\begin{array}{c} 3\\ 1 \\ 2 \\ 1 \\ 0 \\ 0 \\ 0 \\ 6 \\ 7 \\ 6 \\ 7 \\ 6 \\ 7 \\ 6 \\ 7 \\ 6 \\ 7 \\ 7$				

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

