Third Exam
CHEM 256 – Organic Chemistry II
Prof. Bastin
Spring 2016

Name ___________________________ **Section** ________

1. DO NOT START this exam until you are instructed to begin.
2. There are FOURTEEN pages including this cover sheet and the IR frequency and NMR chemical shift tables - make sure they are all here!
3. Provide *CLEAR, CONCISE* answers using unambiquous, carefully drawn structures and mechanisms for the appropriate questions. *Be sure to read each question VERY CAREFULLY.*
4. Do not provide mechanisms for synthesis and product prediction problems.
5. You may only use a pen or pencil and the materials provided in this packet on this exam.
6. If you have papers and/or books with you, they are to be left on the floor **AT THE FRONT OF THE ROOM**. If you need scrap paper please ask.
7. Cell phones must be **OFF and placed on the table at the FRONT of the ROOM**.

1) _______/15 pts

2) _______/14 pts

3) _______/10 pts **Total: ________/100 pts**

4) _______/11 pts

5) _______/12 pts

6) _______/12 pts

7) _______/12 pts

8) _______/14 pts

1) (15 pts) Provide structures for the following compounds.

a) *sec*-butyl alcohol

b) 1-penten-2-ol

c) *cis*-2-methyl-3-propyl-1-cyclohexanone

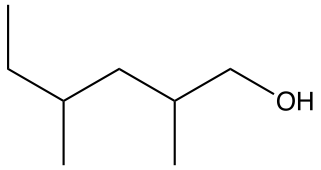
d) *p*-fluoroacetophenone

e) 2,5-diethyloctanal

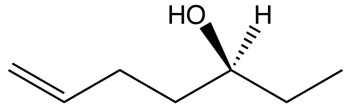
f) 2,4-dihydroxycyclohexane carbaldehyde

2) (14 pts) Provide either common or IUPAC names for the following compounds.

a)



b)



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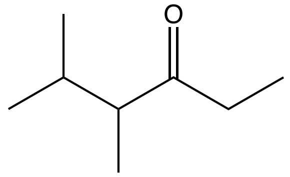

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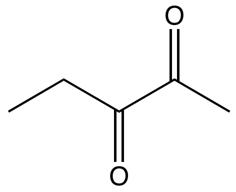

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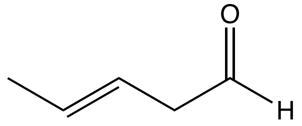

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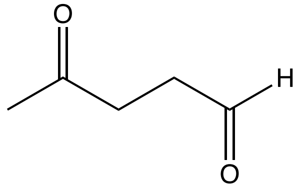
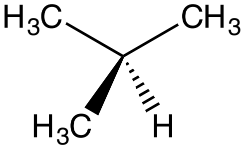


3) (10 pts) Indicate the number of peaks that a ^{13}C-NMR spectrum of each of the following molecules would contain?

a)



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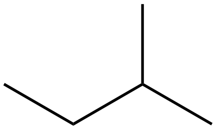

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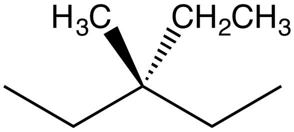

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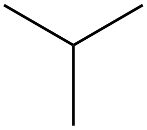

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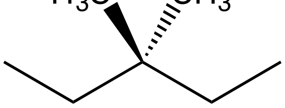
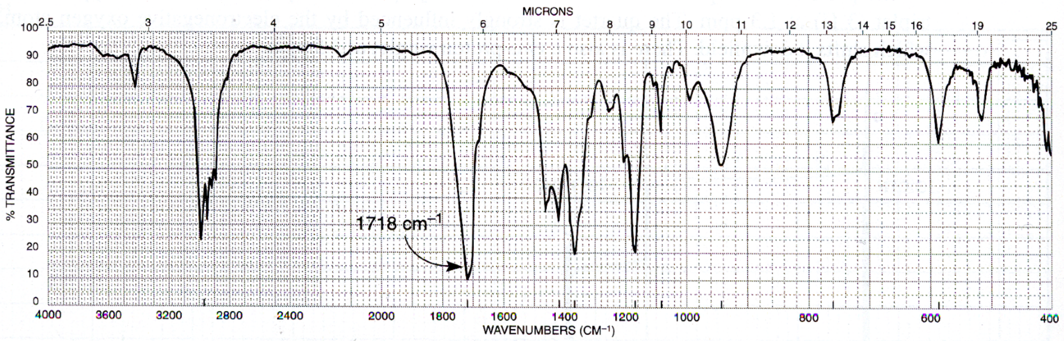


4) (11 pts) Propose a structural formula for compound A, C_4H_8O, consistent with the following ^{1}H-NMR and IR spectra. To receive credit you must justify your structure by assigning ALL the appropriate peaks in the IR and NMR spectra and provide a short narrative describing what structural information each piece of data provided.

b)



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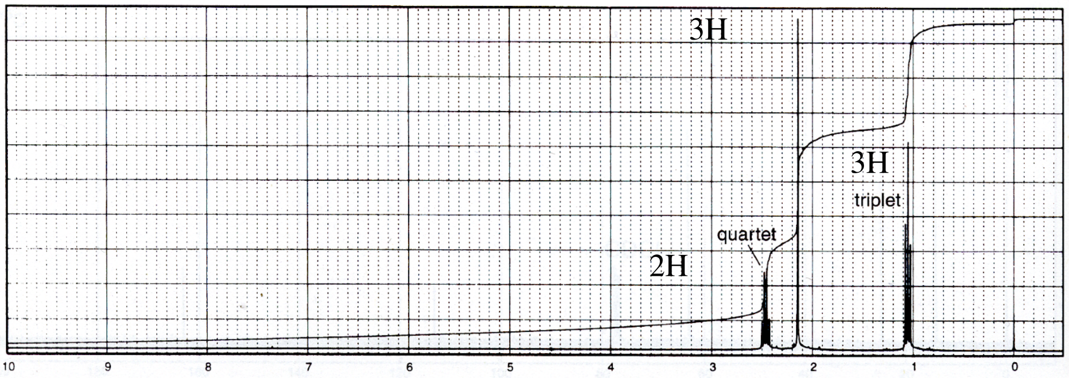
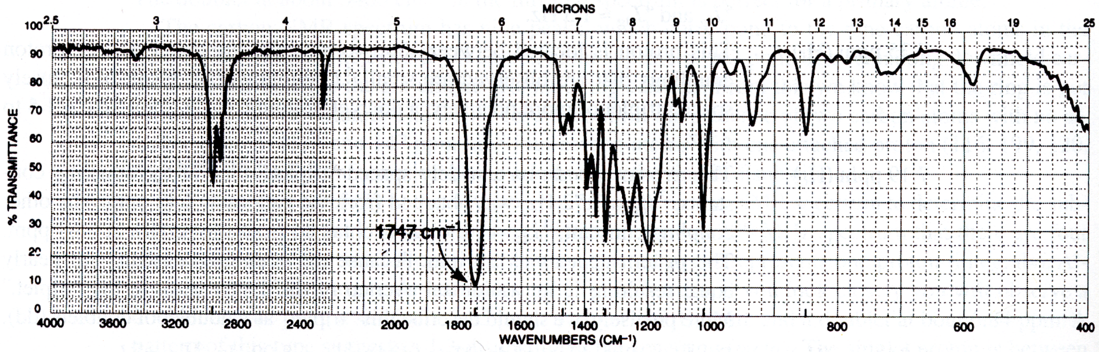
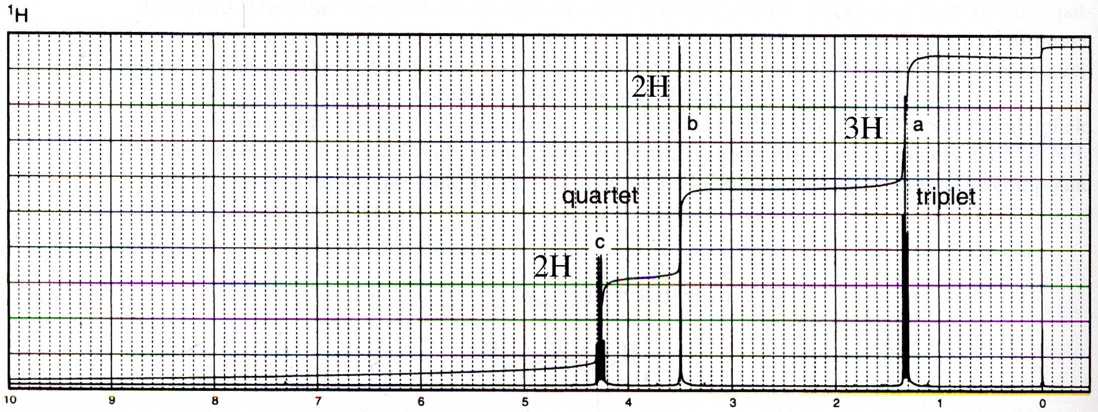
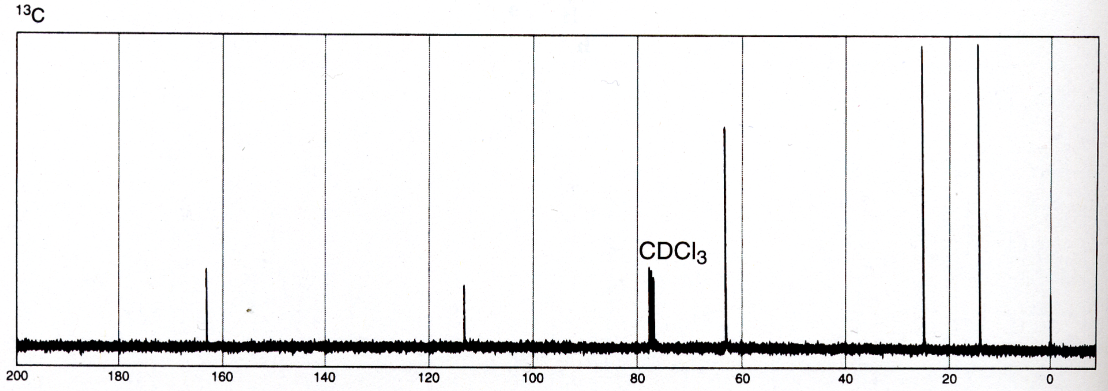


5) (12 pts) Provide the structure of a compound with the molecular formula $C_5H_7NO_2$ using the IR, ^{1}H-NMR, and ^{13}C-NMR provided below. To receive credit you must justify your structure by assigning ALL the appropriate peaks in the IR and NMR spectra and provide a short narrative describing what structural information each piece of data provided.

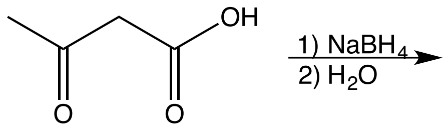






6) (12 pts) Draw the major product(s), if any, of the following reactions. Indicate stereochemistry where relevant.

a)



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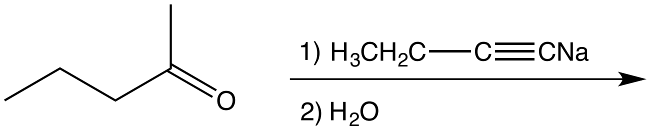

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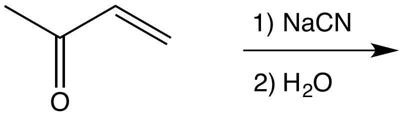

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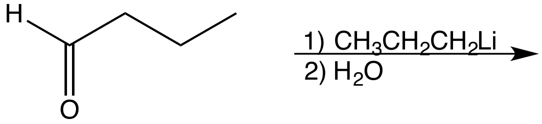
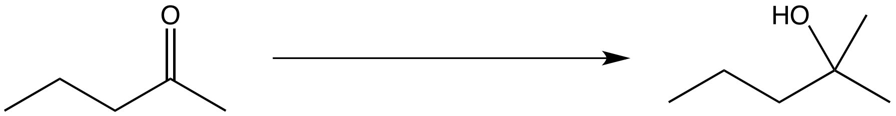


7) (12 pts) Provide the reagent(s) needed to bring about the following transformations.

a)



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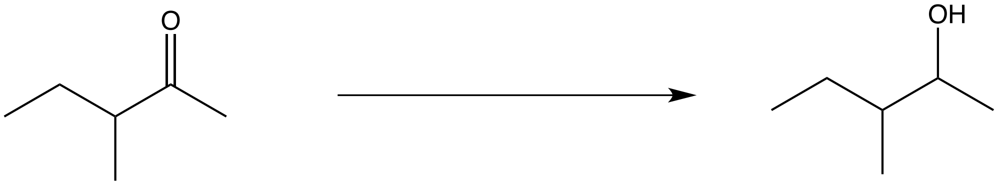

c)

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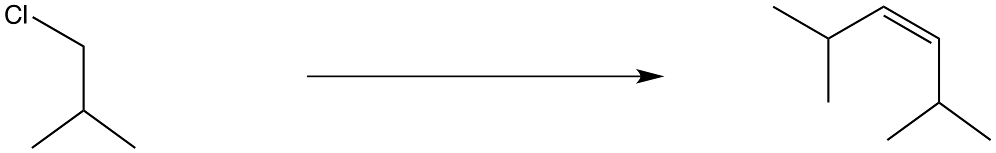
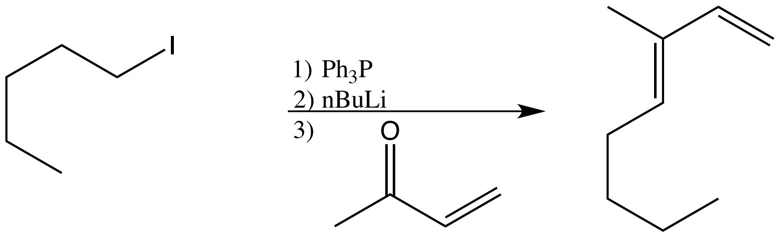


8) (14 pts) Provide a mechanism for the following reaction.



Functional Group	**Frequency (cm^{-1})**	**Intensity and Comments**
Alkanes		
C–H	2980-2850	medium to strong
C–C	1480-1420	medium
Alkenes		
=C–H stretch	3150-3000	medium; very weak for trans
=C–H bend	980-960 (trans)	strong
	730-665 (cis)	strong
C=C	1680-1600	weak to medium
Alkynes		
≡C–H	3350-3300	strong
C≡C	2260-2100	weak to medium
Alkyl halides		
C–Cl	800-600	strong
C–Br	600-500	strong
C–I	500	strong
Alcohols		
O–H	3650-3300	strong and broad
C–O	1350-1050	strong
Amines		
N–H	3500-3100	medium and strong; 1° amines-2 bands; 2° amines-1 band
C–N	~1200	medium
Aromatics		
C–H stretch	3080-3020	weak to medium
C–H bend	900-730	strong
C=C	1650-1580	weak to medium
Carbonyls (C=O)		
Ketones	1730-1700	strong
Aldehydes	1730-1700	strong; also has a O=C-H doublet at ~2700 & 2800 cm^1
Esters	1750-1735	strong; also has C–O stretch
Amides	1680-1630	strong; 1° and 2° amides also have N-H stretch
Acids	1730-1700	strong; also has O–H stretch
Acid Anhydride	1850-1740	strong; doublet
Acid Chlorides	1820-1770	strong
Nitrile (C≡N)	2200-2250	medium
Nitro (NO_2)	Doublet at: 1570-1550 & 1380-1360	strong

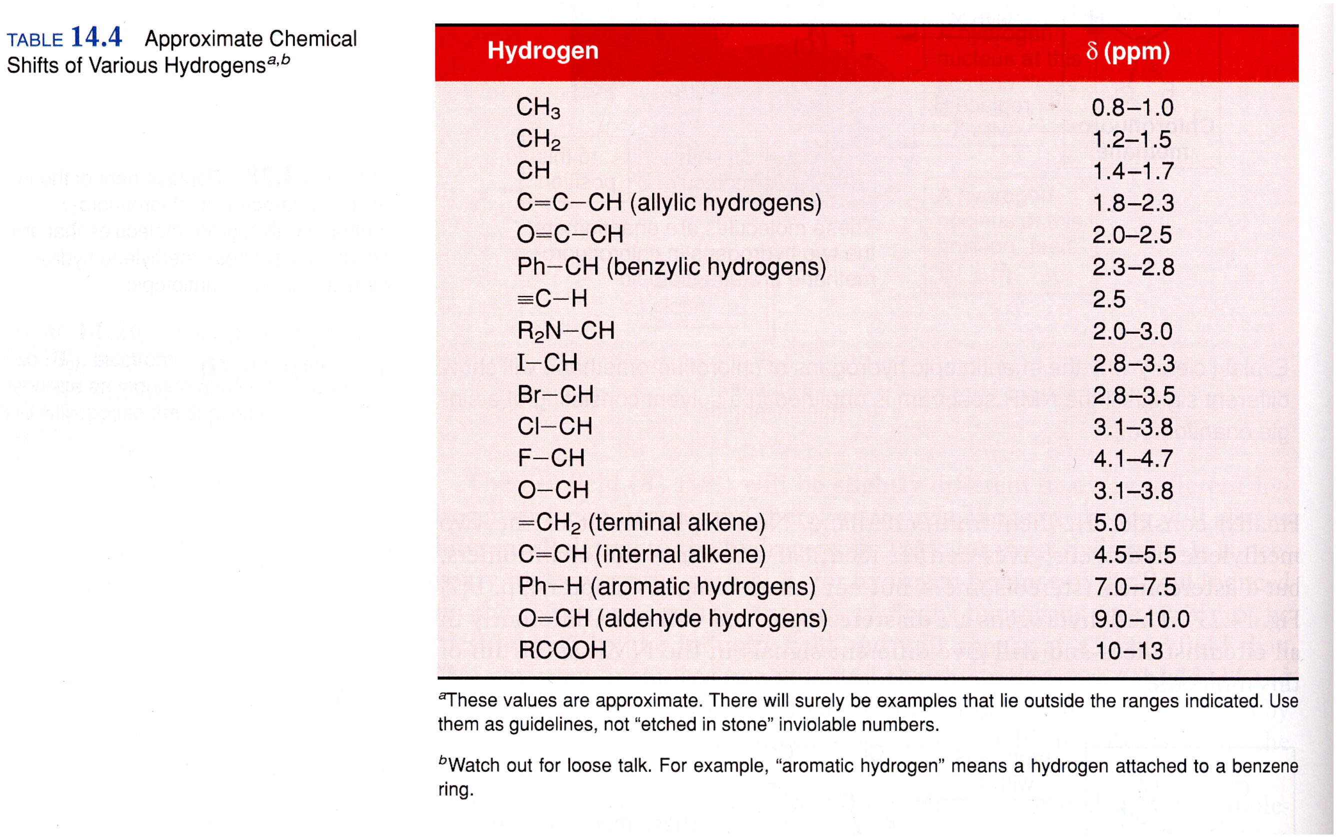


TABLE **14.4** Approximate Chemical Shifts of Various Hydrogens[a,b]

Hydrogen	δ (ppm)
CH_3	0.8–1.0
CH_2	1.2–1.5
CH	1.4–1.7
C=C–CH (allylic hydrogens)	1.8–2.3
O=C–CH	2.0–2.5
Ph–CH (benzylic hydrogens)	2.3–2.8
≡C–H	2.5
R_2N–CH	2.0–3.0
I–CH	2.8–3.3
Br–CH	2.8–3.5
Cl–CH	3.1–3.8
F–CH	4.1–4.7
O–CH	3.1–3.8
=CH_2 (terminal alkene)	5.0
C=CH (internal alkene)	4.5–5.5
Ph–H (aromatic hydrogens)	7.0–7.5
O=CH (aldehyde hydrogens)	9.0–10.0
RCOOH	10–13

[a] These values are approximate. There will surely be examples that lie outside the ranges indicated. Use them as guidelines, not "etched in stone" inviolable numbers.

[b] Watch out for loose talk. For example, "aromatic hydrogen" means a hydrogen attached to a benzene ring.

degrees of unsaturation = (#C atoms) – (#H atoms)/2 + (#N atoms)/2 + 1

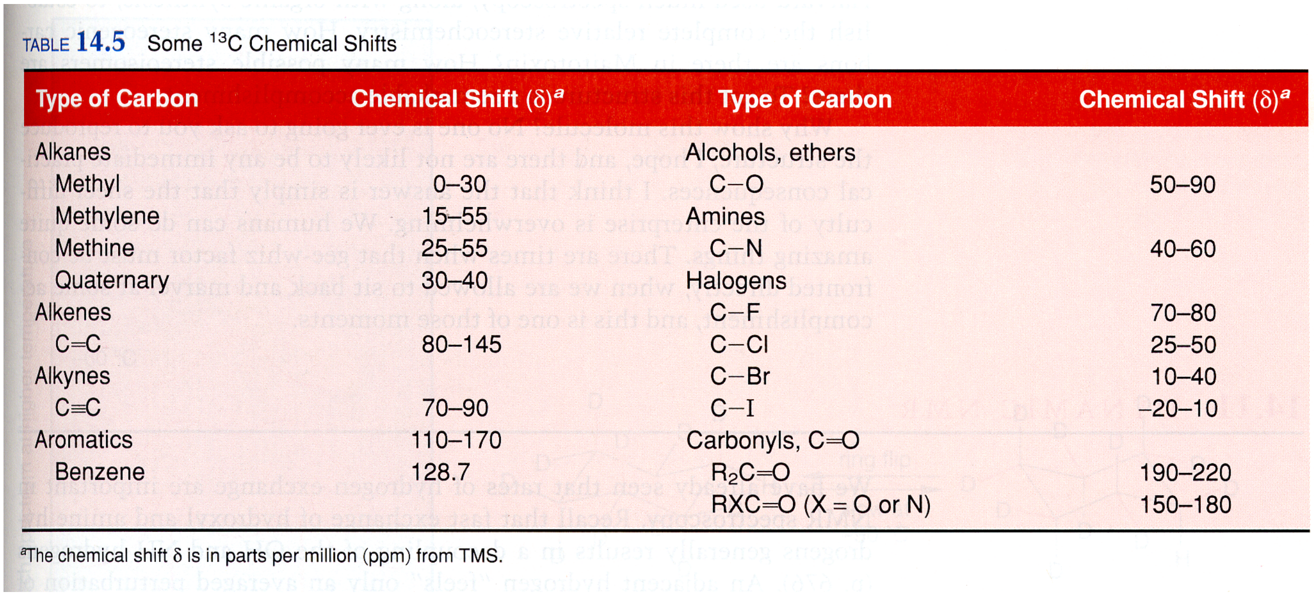


TABLE **14.5** Some ^{13}C Chemical Shifts

Type of Carbon	Chemical Shift (δ)[a]	Type of Carbon	Chemical Shift (δ)[a]
Alkanes		Alcohols, ethers	
Methyl	0–30	C–O	50–90
Methylene	15–55	Amines	
Methine	25–55	C–N	40–60
Quaternary	30–40	Halogens	
Alkenes		C–F	70–80
C=C	80–145	C–Cl	25–50
Alkynes		C–Br	10–40
C≡C	70–90	C–I	−20–10
Aromatics	110–170	Carbonyls, C=O	
Benzene	128.7	R_2C=O	190–220
		RXC=O (X = O or N)	150–180

[a] The chemical shift δ is in parts per million (ppm) from TMS.