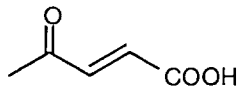
CHEM 3332 - EXAM 3

Bean-Cai. 3
chem 3332

A. Nomenclature (3 points each; 9 total points)

Please provide an acceptable name for each of the following compounds, noting stereochemistry where appropriate.

1.



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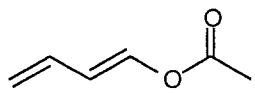
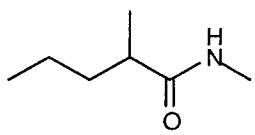
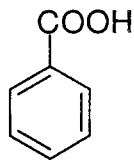


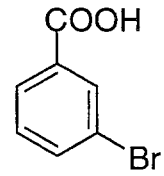
3.



B. Facts (3 points each; 18 total points)

1. Rank the pKa value of the following benzoic acids from lowest (**1**) to highest (**3**).





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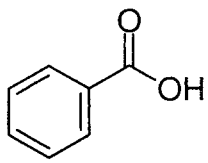
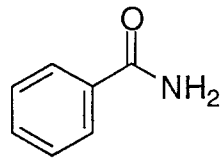
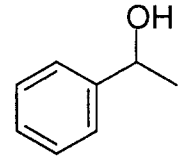
2. Rank the boiling points of the following molecules from lowest (**1**) to highest (**3**).







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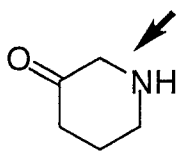
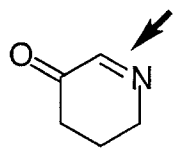
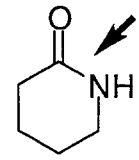
3. Rank the indicated C-N bond lengths from shortest (**1**) to longest (**3**).







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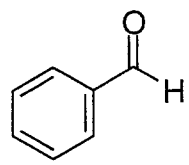
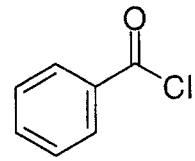
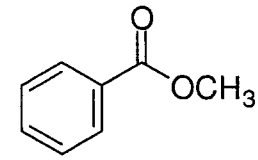
4. Rank these molecules from slowest (**1**) to fastest (**3**) in their rate of nucleophilic acyl substitution.







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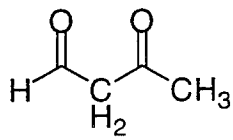
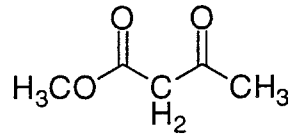
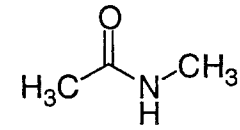
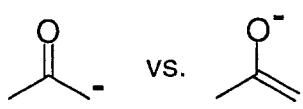
5. Circle **only** the most acidic hydrogen or hydrogens on each of the following molecules (i.e., one circle per molecule).

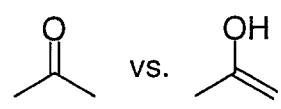


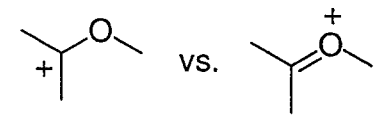




6. Circle the more stable structure in each of the following pairs (i.e., one circle for each pair of structures).

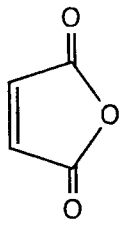






C. Reactions: Total = 30 points, 6 points each
Please provide the starting material, the reagents, or major product in the answer box.
Be sure your drawing indicates stereochemistry if applicable. Partial credit is awarded only when intermediate products are shown below the reaction.

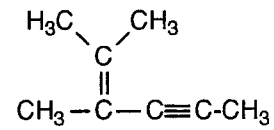
1.



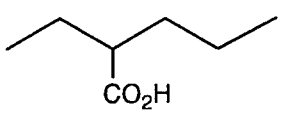
1. $(CH_3)_2NH$
2. H^+
3. $SOCl_2$
4. CH_3CH_2OH
5. $LiAlH_4$ (xs)
6. H_2O

2.

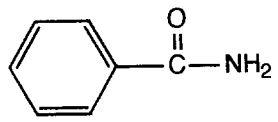
1. $CH_3C{\equiv}C^-Na^+$
2. H_3O^+
3. PCC
4. $Ph_3P{=}C(CH_3)_2$



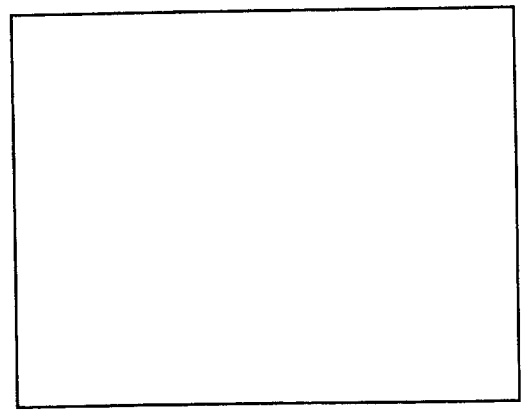
3.

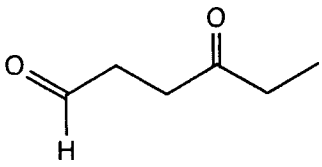


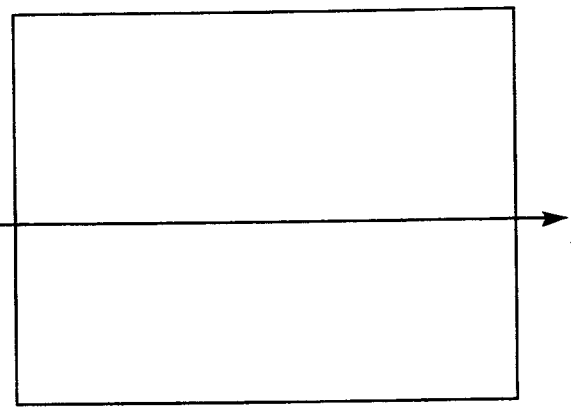
1. CH_3CH_2Li (2 eq)
2. H_3O^+
3. $NaCN/H^+$ or HCN
4. $LiAlH_4$
5. H_2O

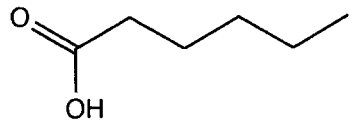
4. 

1. $SOCl_2$ or $POCl_3$
2. CH_3CH_2MgBr
3. H_3O^+
4. Br_2/acetic acid



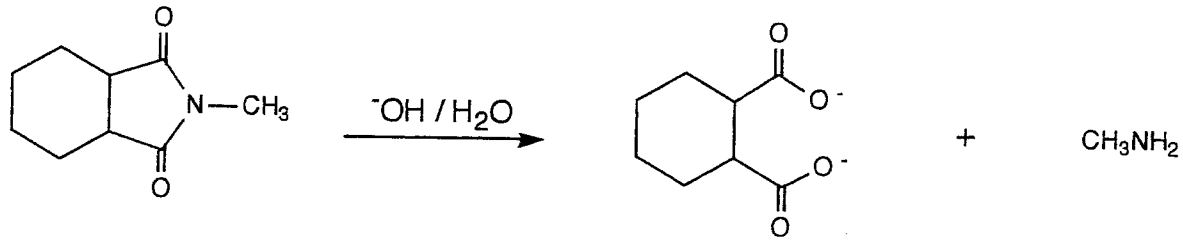
5. 

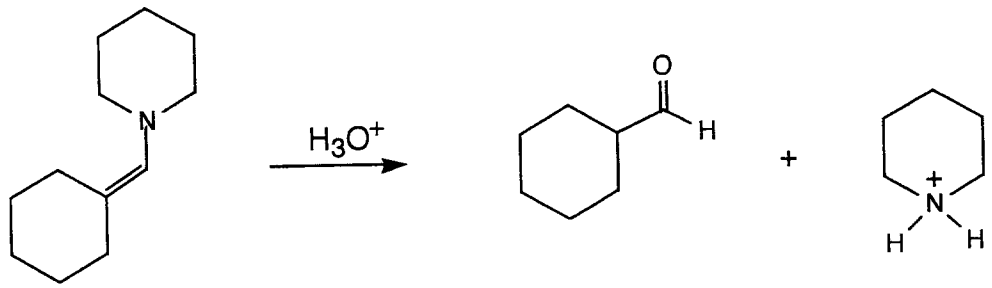




D. Mechanism: Total = 18 points (9 points each)

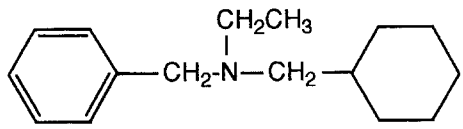
Provide clear mechanisms for reactions 1 and 2. Use curved arrow notaton to indicate "electron flow." **Show all intermediates and all formal charges.** If there is more than one resonance structure, you must show the "best" (i.e. lowest energy) structure.

1. 

2. 

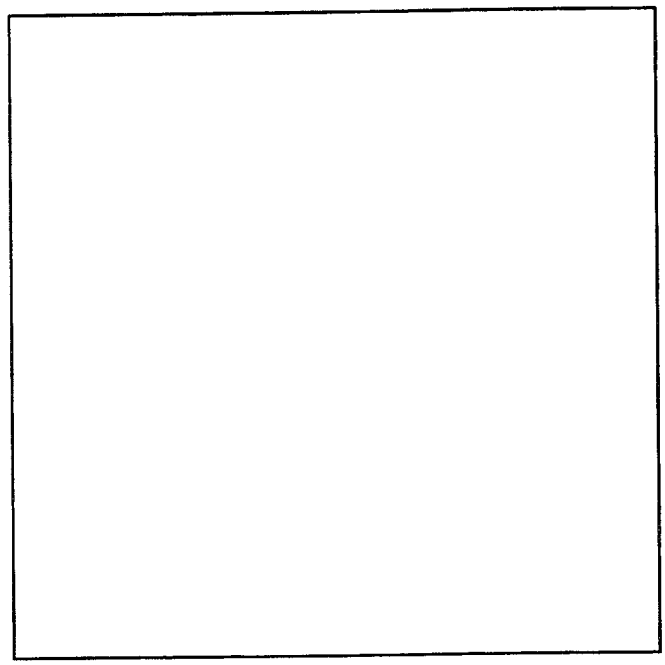
E. Synthesis: 15 Points

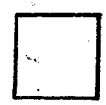
Synthesize the molecule below using any of the following reagents: benzene, cyclohexane, alcohols, alkanes, alkenes, and/or alkynes of **two carbons or less**, any inorganic reagents, any oxidizing or reducing agents, and any peroxyacids.

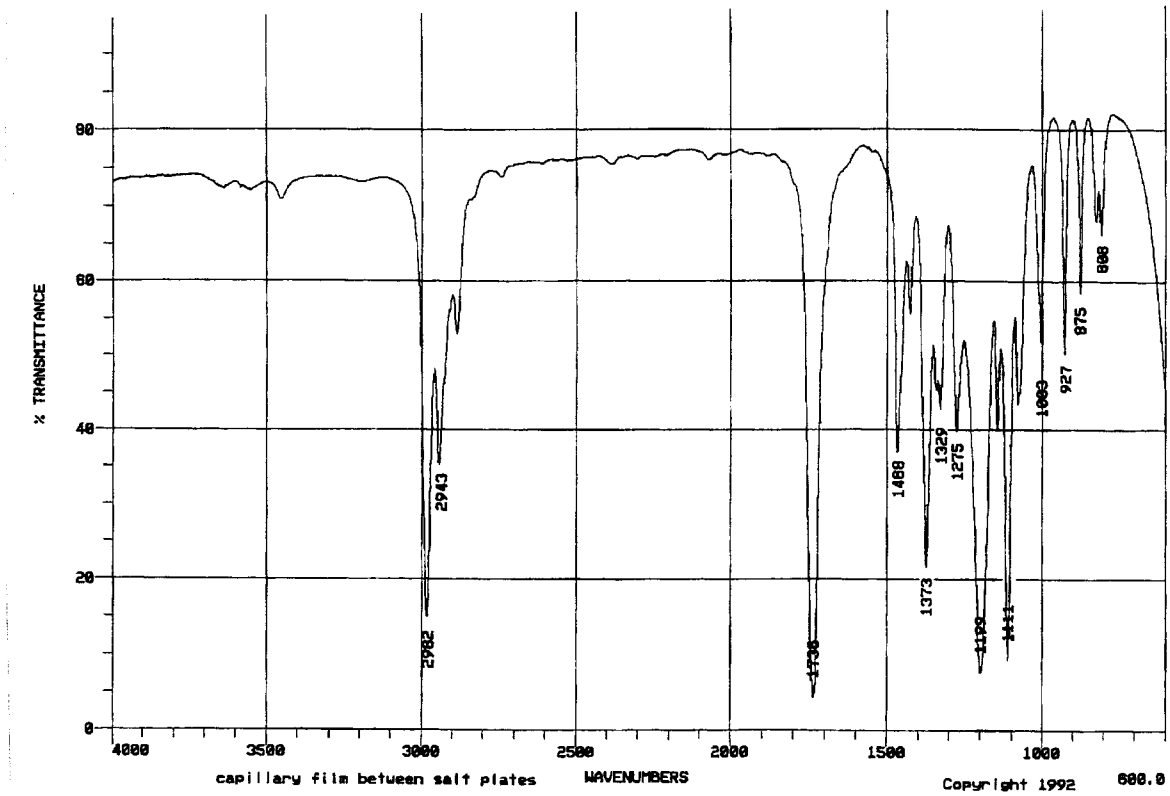


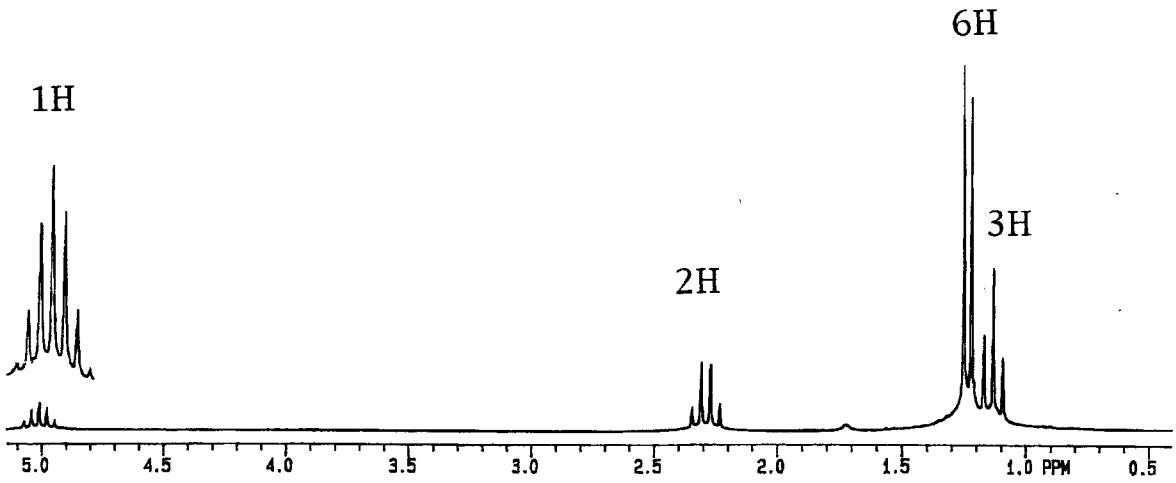
F. Spectroscopy: 10 Points

A compound with the formula $\mathbf{C_6H_{12}O_2}$ exhibits the IR, ^{1}H NMR, and proton-decoupled ^{13}C NMR spectra shown on the following page. Please identify this compound and draw the structure in the box provided below.






% TRANSMITTANCE
90
60
40
20
0
4000
3500
3000
2500
2000
1500
1000
2943
1488
1373
1329
1275
927
875
808
capillary film between salt plates
WAVENUMBERS
Copyright 1992
600.0


1H
2H
6H
3H
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0 PPM
0.5

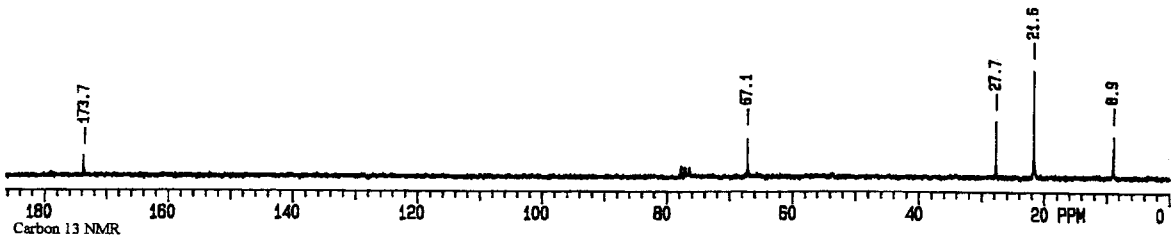

173.7
67.1
27.7
21.5
8.9
180
160
140
120
100
80
60
40
20 PPM
0
Carbon 13 NMR

TABLE 13.2 Characteristic infrared absorptions of groups

GROUP		FREQUENCY RANGE (cm^{-1})	INTENSITY[a]
A. Alkyl			
C—H (stretching)		2853–2962	(m–s)
Isopropyl, $—CH(CH_3)_2$		1380–1385	(s)
	and	1365–1370	(s)
tert-Butyl, $—C(CH_3)_3$		1385–1395	(m)
	and	~1365	(s)
B. Alkenyl			
C—H (stretching)		3010–3095	(m)
C=C (stretching)		1620–1680	(v)
R—CH=CH_2	(out-of-plane C—H bendings)	985–1000	(s)
	and	905–920	(s)
$R_2C=CH_2$		880–900	(s)
cis-RCH=CHR		675–730	(s)
trans-RCH=CHR		960–975	(s)
C. Alkynyl			
≡C—H (stretching)		~3300	(s)
C≡C (stretching)		2100–2260	(v)
D. Aromatic			
Ar—H (stretching)		~3030	(v)
Aromatic substitution type (C—H out-of-plane bendings)			
Monosubstituted		690–710	(very s)
	and	730–770	(very s)
o Disubstituted		735–770	(s)
m Disubstituted		680–725	(s)
	and	750–810	(very s)
p Disubstituted		800–840	(very s)
E. Alcohols, Phenols, and Carboxylic Acids			
O—H (stretching)			
Alcohols, phenols (dilute solutions)		3590–3650	(sharp, v)
Alcohols, phenols (hydrogen bonded)		3200–3550	(broad, s)
Carboxylic acids (hydrogen bonded)		2500–3000	(broad, v)
F. Aldehydes, Ketones, Esters, and Carboxylic Acids			
C=O (stretching)		1630–1780	(s)
Aldehydes		1690–1740	(s)
Ketones		1680–1750	(s)
Esters		1735–1750	(s)
Carboxylic acids		1710–1780	(s)
Amides		1630–1690	(s)
G. Amines			
N—H		3300–3500	(m)
H. Nitriles			
C≡N		2220–2260	(m)

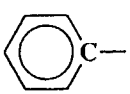
[a] Abbreviations: s = strong, m = medium, w = weak, v = variable, ~ = approximately.

TABLE 13.3 Approximate proton chemical shifts

TYPE OF PROTON	CHEMICAL SHIFT (δ, ppm)
1° Alkyl, RCH_3	0.8–1.0
2° Alkyl, RCH_2R	1.2–1.4
3° Alkyl, R_3CH	1.4–1.7
Allylic, $R_2C{=}C(R){-}CH_3$	1.6–1.9
Ketone, $RC(=O)CH_3$	2.1–2.6
Benzylic, $ArCH_3$	2.2–2.5
Acetylenic, $RC{\equiv}CH$	2.5–3.1
Alkyl iodide, RCH_2I	3.1–3.3
Ether, $ROCH_2R$	3.3–3.9
Alcohol, $HOCH_2R$	3.3–4.0
Alkyl bromide, RCH_2Br	3.4–3.6
Alkyl chloride, RCH_2Cl	3.6–3.8
Vinylic, $R_2C{=}CH_2$	4.6–5.0
Vinylic, $R_2C{=}CH(R)$	5.2–5.7
Aromatic, ArH	6.0–9.5
Aldehyde, $RC(=O)H$	9.5–9.6
Alcohol hydroxyl, ROH	0.5–6.0[a]
Amino, $R{-}NH_2$	1.0–5.0[a]
Phenolic, ArOH	4.5–7.7[a]
Carboxylic, $RC(=O)OH$	10–13[a]

[a] The chemical shifts of these protons vary in different solvents and with temperature and concentration.

TABLE 13.4 Approximate carbon-13 chemical shifts

TYPE OF CARBON ATOM	CHEMICAL SHIFT (δ, ppm)
1° Alkyl, RCH_3	0–40
2° Alkyl, RCH_2R	10–50
3° Alkyl, $RCHR_2$	15–50
Alkyl halide or amine, $-\overset{|}{C}-X$ (X = Cl, Br, or $-\overset{|}{N}-$)	10–65
Alcohol or ether, $-\overset{|}{C}-O$	50–90
Alkyne, $-C{\equiv}$	60–90
Alkene, $>C{=}$	100–170
Aryl, 	100–170
Nitriles, $-C{\equiv}N$	120–130
Amides, $-C(=O)-N-$	150–180
Carboxylic acids, esters, $-C(=O)-O$	160–185
Aldehydes, ketones, $-C(=O)-$	182–215