Circle one: I wish to have my exam put in the rack. I wish to pick up my exam.

Printed Name_____.
(Please print clearly)

Signature_____.

CHEMISTRY 262

Final May 8, 2013
200 Points 8:00-10:00 AM

This exam has 9 problems on pages 2 through 11.

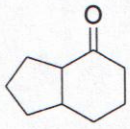
RULES

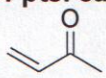
1. The use of a calculator and model kits are **not** permitted.
2. This exam is closed book and closed note. No aids other than writing implements are permitted.
3. Answer the questions in the spaces provided on this exam.
4. If you wish to ask a question about procedures or about a problem on the exam, raise your hand.

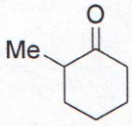
1. _____
2. _____
3. _____
4. _____
5. _____
6. _____
7. _____
8. _____
9. _____

TOTAL: /200

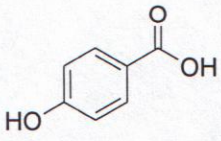
1. Predict the major product or products that you would expect to be formed in **ten** of the following fifteen reactions. If you feel that no reaction will occur, then answer no reaction. Be sure to answer **only** ten problems. If you answer more than ten, then *only your first ten will be graded.* (**40 points/ 4 pts. each**)

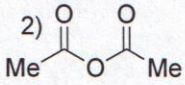
(a) 

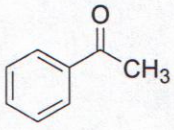
1)  , NaOMe
MeOH, heat
2) $Ph_3P{=}CHCO_2Me$

(b) 

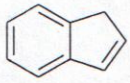
a) LDA, THF
b) MeI

(c) 

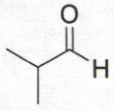
1) CH_2N_2
2) 

(d) 

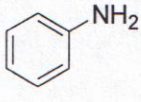
1) NaOH, excess I_2
2) $(COCl)_2$, Na_2CO_3
3) $LiAlH(O^tBu)_3$

(e) 

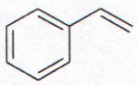
1) a. O_3
b. Me_2S
2) NH_3, $NaCNBH_3$

(f) 

1) NH_3, H^+, KCN
2) H^+, H_2O

(g) 

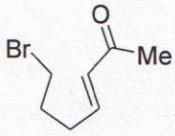
1) HO-N=O, H_2SO_4
2) CuCN
3) MeMgBr
4) H^+, H_2O

(h) 

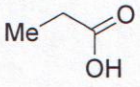
1) a. BH_3, THF
b. PCC, CH_2Cl_2
2) NH_2OMe

(i) 

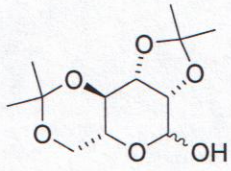
1) a. n-BuLi
b. MeI
2) a. n-BuLi
b. CH_2=CH-CH_2Br
3) H^+, H_2O, $HgCl_2$

(j) 

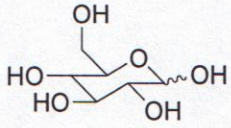
^tBu-SLi

(k) 

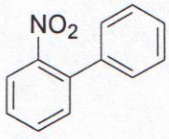
1) a. PBr_3, Br_2
b.water workup
2) excess NH_3

(l) 

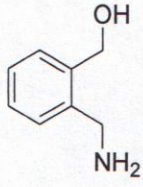
Ph_3P=CHOMe
(LiBr present)

(m) 

1) Br_2, H_2O
2) $Fe_2(SO_4)_3$
H_2O_2

(n) 

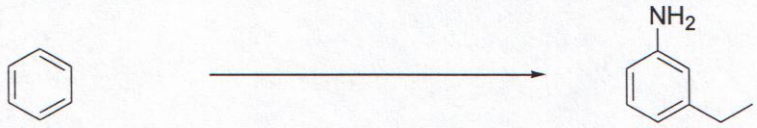
SO_3, H_2SO_4

(o) 

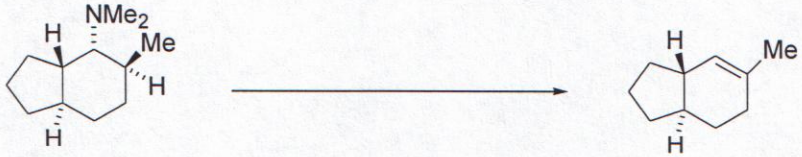
PCC (2 equiv.)
CH_2Cl_2

2. Fill in the reagents needed for accomplishing **five** of the eight following transformations. More than one step may be required. Be sure to answer **only** five problems. If you answer more than five problems, then *only your first five will be graded.* (**20 points/ 4 pts. each**)

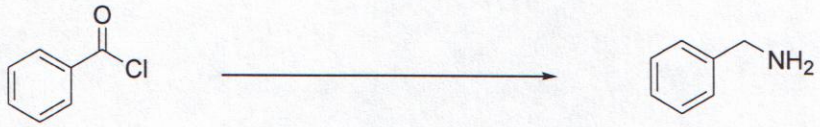
a)



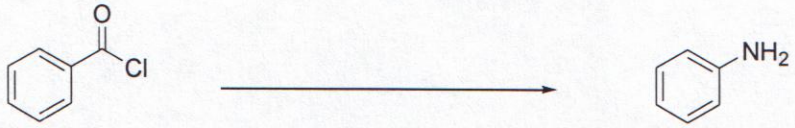
b)



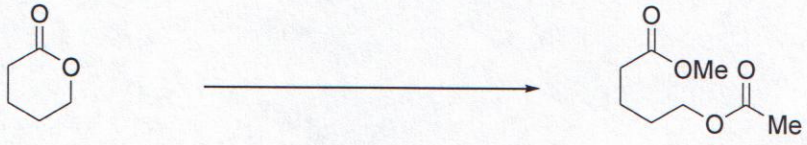
c)



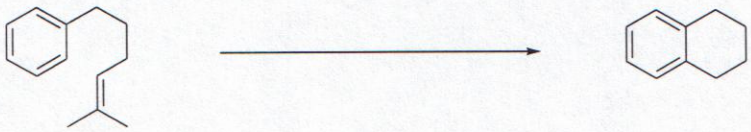
d)



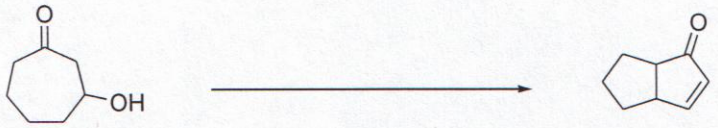
e)



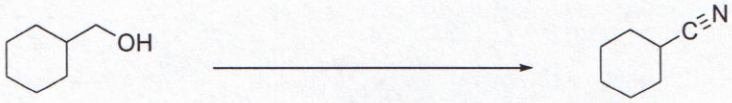
f)



g)



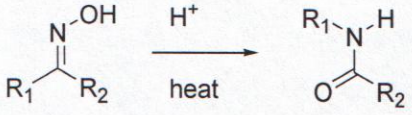
h)



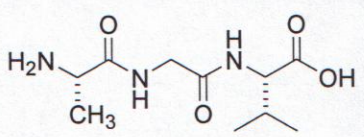
3. **a.** The carbonyl C=O stretch of an amide is at 1650 cm^{-1} and the carbonyl C=O stretch of an ester is 1740 cm^{-1}, an observation that indicates that the carbonyl of an amide is weaker than that of an ester. So why are amides more stable than esters? Be sure to support your answer with a picture. (**5 points**)

b. Based on your argument above, would you expect the ester or the amide to have the most intense stretch in an IR? Why? (**5 points**)

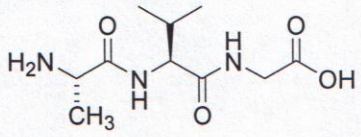
c. Amide stability can be the driving force for reactions like the Beckmann rearrangement illustrated below. In this reaction, R_1 migrates in preference to R_2. Why? Please note that you do not need to write a mechanism for the reaction. Just explain the initial migration step and support your answer with an appropriate drawing. (**5 points**)



4. Several years ago a student made the pair of peptides shown below.



A

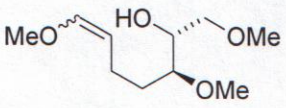


B

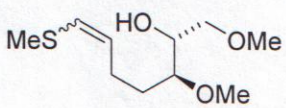
a. Unfortunately, the labels on the vials got old and fell off. How would you use a mass spectrometer to tell the difference between the two peptides? (**10 points**)

b. If you had to resynthesize peptide **A**, then how would you do it starting from the substrate below (the grey dot is Merrifield's resin) and any amino acid precursors and reagents that you need (**15 points**).

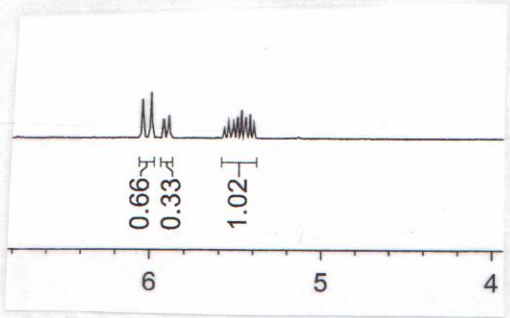
5. In the following scheme, an NMR spectrum is shown for each of the two molecules illustrated.

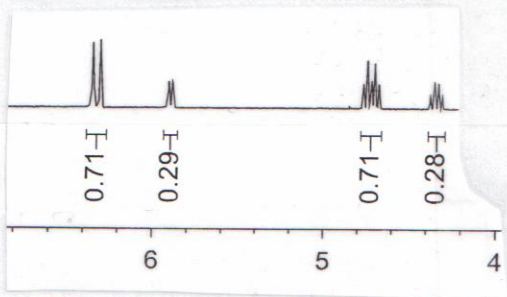


A



B



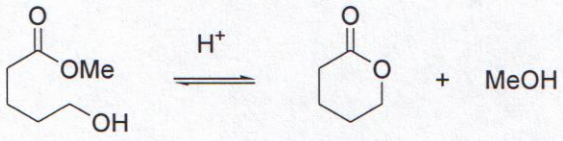


a. Draw arrows on the Scheme above that indicate which spectrum goes with which molecule. How do you know? Please support your answer with a picture. (**5 points**)

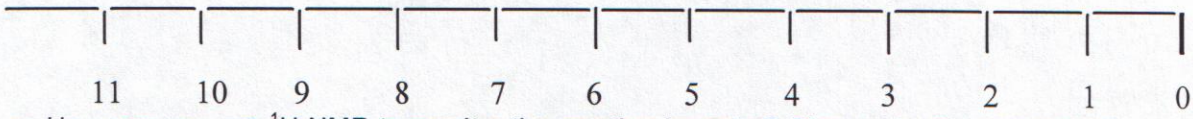
b. Is the double bond that gives rise to either spectrum mostly present cis or trans? Please note that for these spectra the integrations are given as numbers (0.71, 0.29, etc.). Explain how you made your assignment? (**5 points**)

c. Draw a splitting tree that explains the pattern found in the NMR on the right at approximately 4.8 ppm. (**5 points**)

6. **a.** Please draw a "curved-arrow" mechanism for the following reaction. (**5 points**)

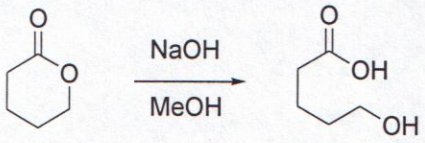


b. Draw the ^{1}H NMR spectrum that you would expect for the starting material. (**5 points**)

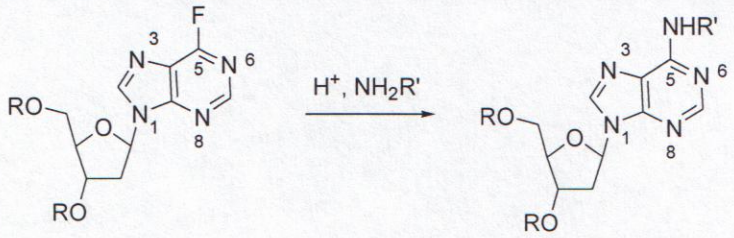


c. How can you use ^{1}H NMR to monitor the reaction in part a? Please identify one change in the spectrum that you could monitor other than the loss of the alcohol proton since OH protons in an NMR can often be difficult to assign. (**5 points**)

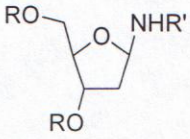
d. The equilibrium shown in part a is favored thermodynamically (entropy). In spite of this observation, the reaction illustrated below does proceed nicely to the product even when MeOH is used as solvent. Why? (**5 points**)



7. a. Write a "curved-arrow" mechanism for the following reaction. (**10 points**)



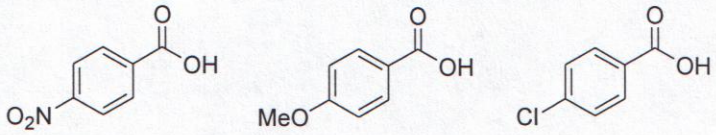
b. The reaction can lead to the side-product illustrate below. Write a "curved-arrow" mechanism that illustrates how this side-product can form. (**10 points**)

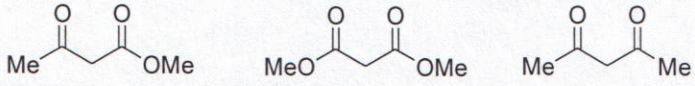


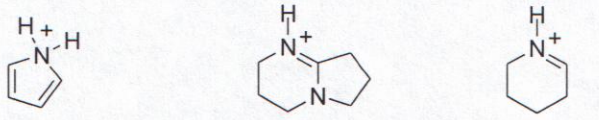
c. The fluoride in the starting material was in place of a potential Cl-leaving group in order to minimize the side-reaction. The idea was to use the more electronegative fluorine in order to make C_5 in the starting material more electron poor and hence more susceptible to nucleophilic attack. How would you use ^{13}C NMR to determine if this idea was accurate? (**5 points**)

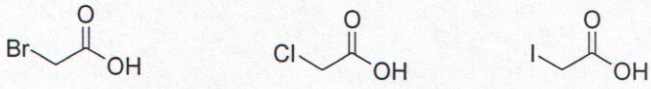
d. Protonation of the starting material can happen readily at N_3, N_6, and N_8 but not N_1. Why? (**5 points**)

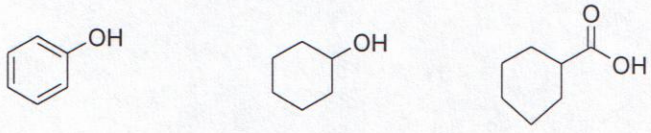
8. Rank the following molecules in terms of acidity from the most acidic (**1**) to the least acidic proton (**3**). (**15 points/ 3 pts each**)

a) 

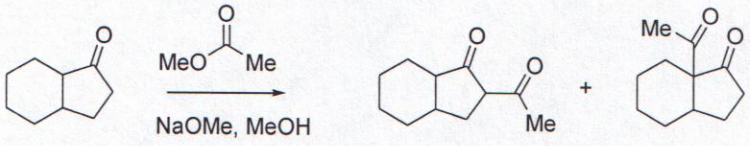
b) 

c) 

d) 

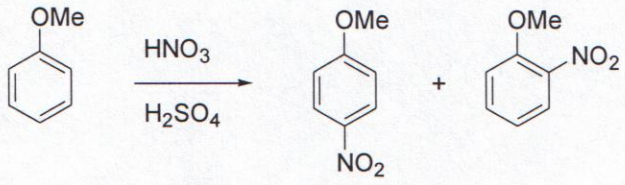
e) 

9. a. In the reaction below, product **1** is formed. Is this an example of kinetic or thermodynamic control? Explain. (**5 points**)



1 **2**

b. Why does the reaction below lead to mainly ortho and para products? (**5 points**)



c. How could you use a ^{13}C NMR to quickly tell if the major product formed in part b is the para or ortho product. (**5 points**)

d. Since I asked you to memorize your DNA bases, please draw the structure for a GC base pair. Please show the bases and the hydrogen bonds. You do not have to show the sugars. (**5 points**)

PERIODIC TABLE OF THE ELEMENTS

1																	2
H																	He
1.0079																	4.0026
3	4											5	6	7	8	9	10
Li	Be											B	C	N	O	F	Ne
6.941	9.0122											10.811	12.011	14.007	15.999	18.998	20.180
11	12											13	14	15	16	17	18
Na	Mg											Al	Si	P	S	Cl	Ar
22.990	24.305											26.982	28.086	30.974	32.066	35.453	39.948
19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
39.098	40.078	44.956	47.88	50.942	51.996	54.938	55.847	58.933	58.69	63.546	65.39	69.723	72.61	74.922	78.96	79.904	83.80
37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
85.468	87.62	88.906	91.224	92.906	95.94	(98)	101.07	102.91	106.42	107.87	112.41	114.82	118.71	121.75	127.60	126.90	131.29
55	56	71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86
Cs	Ba	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
132.91	137.33	174.97	178.49	180.95	183.85	186.21	190.2	192.22	195.08	196.97	200.59	204.38	207.2	208.98	(209)	(210)	(222)
87	88	103	104	105	106	107	108	109	110	111							
Fr	Ra	Lr	Unq	Unp	Unh	Uns	Uno	Une	Uun	Uuu							
(223)	(226)	(260)	(261)	(262)	(263)	(262)	(265)	(266)	(269)	(272)							

TABLE 11-4

Isotopic composition of some common elements

Element	M^+		M+1		M+2	
hydrogen	^{1}H	100.0%				
carbon	^{12}C	98.9%	^{13}C	1.1%		
nitrogen	^{14}N	99.6%	^{14}N	0.4%		
oxygen	^{16}O	99.8%			^{16}O	0.2%
sulfur	^{32}S	95.0%	^{32}S	0.8%	^{34}S	4.2%
chlorine	^{35}Cl	75.5%			^{37}Cl	24.5%
bromine	^{79}Br	50.5%			^{81}Br	49.5%
iodine	^{126}I	100.0%				

TABLE 11-3

"Exact" Masses of Common Isotopes

Isotope	*Atomic Mass (amu)*
^{12}C	12.000000
^{1}H	1.007825
^{16}O	15.994914
^{14}N	14.003050

57	58	59	60	61	62	63	64	65	66	67	68	69	70
La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb
138.9	140.1	140.9	144.2	(145)	150.4	152.0	157.3	158.9	162.5	164.9	167.3	168.9	173.0
89	90	91	92	93	94	95	96	97	98	99	100	101	102
Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No
(227)	232.04	231.04	238.03	(237)	(244)	(243)	(247)	(247)	(251)	(252)	(257)	(258)	(259)