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

Exam III
100 Points

March 27, 2013
6:30 – 8:30 PM

This exam has 8 problems on pages 2 through 8.

RULES

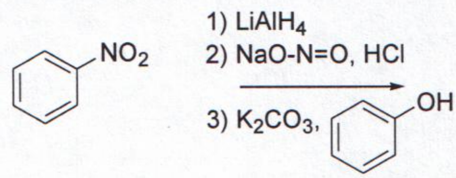
1. The use of a calculator and model kits are **not** permitted.
2. This exam is closed book and closed note. No aids other than writing implements are permitted.
3. Answer the questions in the spaces provided on this exam.
4. If you wish to ask a question about procedures or about a problem on the exam,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

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

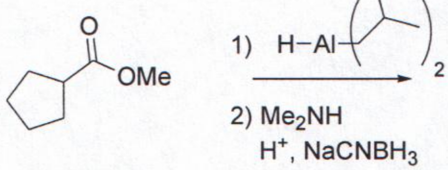
TOTAL: /100

1. Predict the major product or products (be inclusive) that you would expect to be formed in **seven** of the following ten reactions (continued on the next page). If you feel that no reaction will occur, then answer no reaction. You may assume a workup step for each reaction. Be sure to answer **only** seven problems. If you answer more than seven, then *only your first seven will be graded.* (**21 points/ 3 pts. each**)

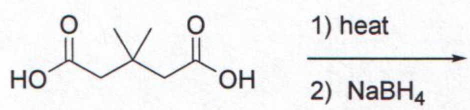
(a)



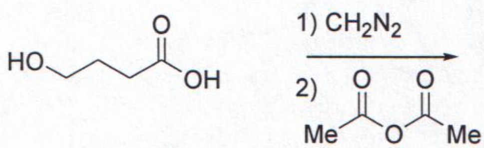
(b)



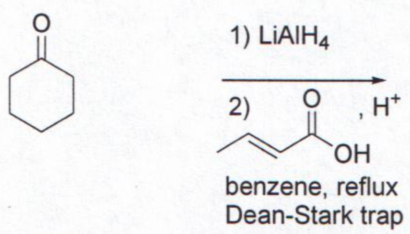
(c)



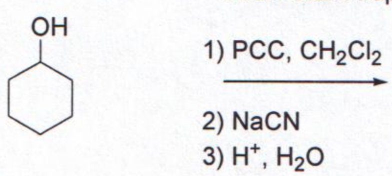
(d)



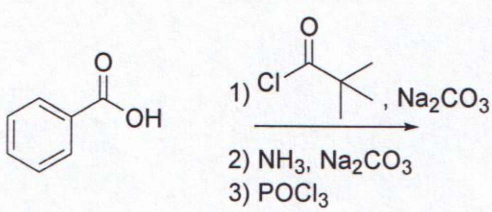
(e)

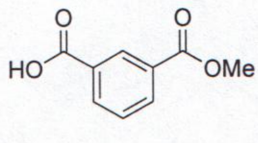


(f)



(g)

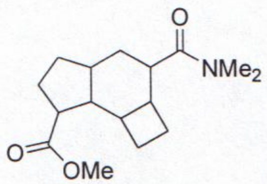


(h) 

1) $BH_3 \cdot THF$

2) DIBAL-H

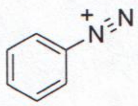
3) H^+, H_2O (workup)

(i) 

1) NaOH (1 equiv.) MeOH

2) $(COCl)_2$, Na_2CO_3

3) $PhCH_2SH$, Na_2CO_3

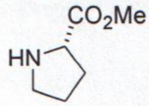
(j) 

1) CuBr

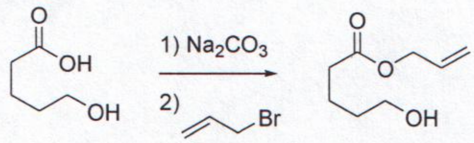
2) Mg(0)

3) CO_2 (followed by workup)

4) $SOCl_2$, heat

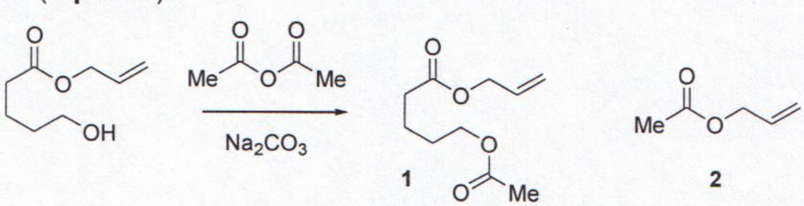
5) 

2. Consider the following reaction.

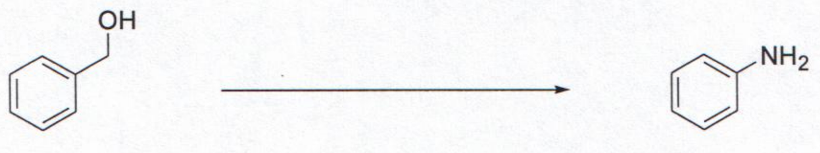


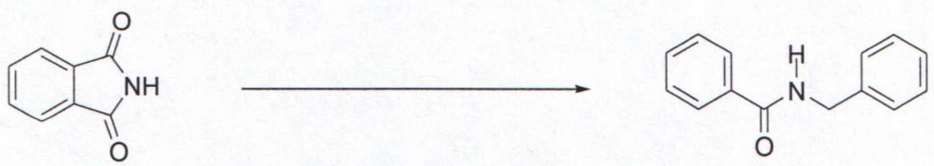
a. Why does this reaction lead to the formation of an ester product rather than an ether product derived from the alcohol. (**5 points**)

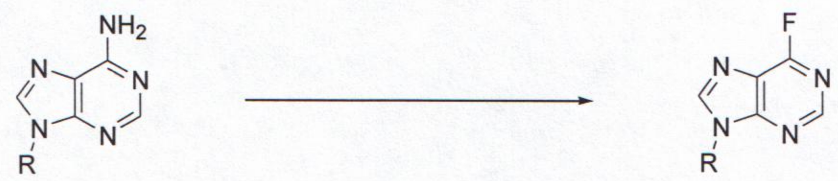
b. The product from the reaction above was left overnight before trying to use it to make product **1** as illustrated below. This led to the formation of product **2** instead of **1**. What happened? (**5 points**)

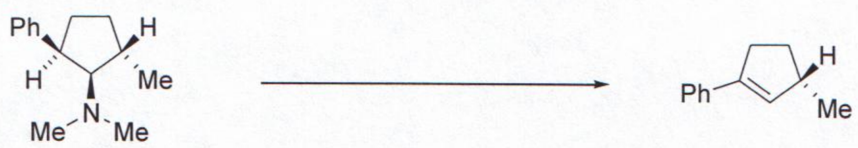


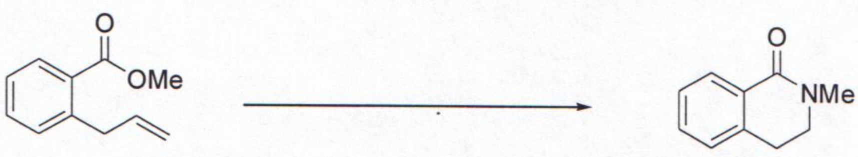
3. Fill in the reagents needed for accomplishing **three** of the five following transformations. More than one step may be required. Be sure to answer **only** three problems (**9 points/ 3 pts. each**)

a) 

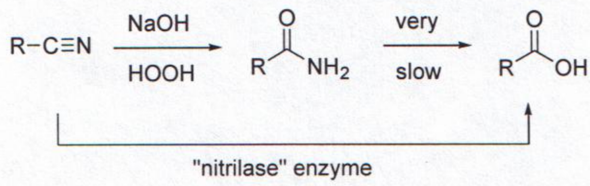
b) 

c) 

d) 

e) 

4. Consider the following:



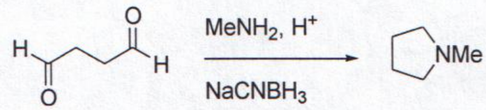
a. Write a "curved-arrow" mechanism for the first step (NaOH, HOOH) of the sequence. (**5 points**)

b. The reaction can be used to make the amide because the second step leading to the acid is very slow. Why? Use a picture to help explain. (**5 points**)

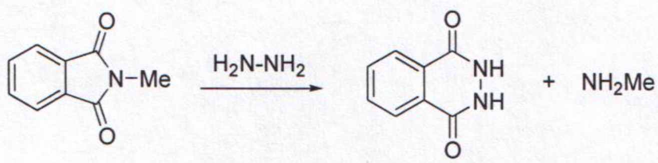
c. Enzymes called nitrilases convert nitriles all the way to acids. What is present in their active sites that allows for this to happen readily at room temperature? Again, use a picture to help explain your answer (**5 points**)

5. Provide a "curved-arrow" mechanism for each of the transformations illustrated below.

a. (5 points)



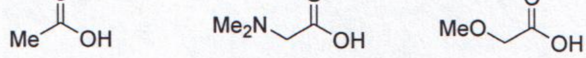
b. (5 points)



c. Hydrazine is used for the reaction shown in part b because it is an outstanding nucleophile; a much better nucleophile than ammonia. Why is hydrazine such a good nucleophile? (**5 points**)

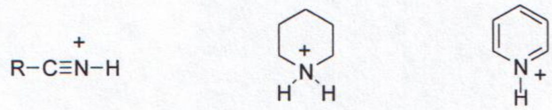
6. Rank the following molecules in terms of the acidity of the proton on either the oxygen or nitrogen. Rank the most acidic proton **1** and the least acidic proton **3**. (**10 points/ 2 pts each**)

a)



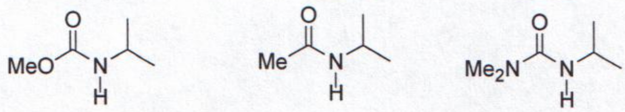
___ ___ ___

b)



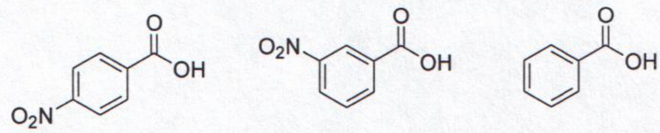
___ ___ ___

c)



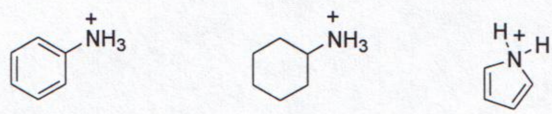
___ ___ ___

d)



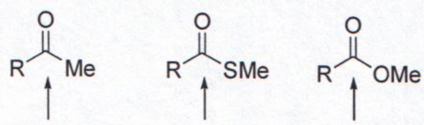
___ ___ ___

e)



___ ___ ___

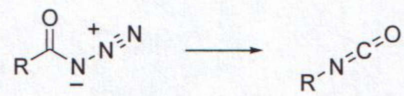
7. a. Nature often activates a carboxylic acid toward nucleophilic attack by converting it to a thioester. Use the NMR data provided below to explain why a thioester is more reactive toward a strong nucleophile than a norm al ester. (**5 points**)



200 - 210 ppm   197 ppm   170-180 ppm

b. The thioester is also activated for reactions with weak nucl eophiles. Why? (**5 points**)

8. a. In the Curtius rearrangement an acyl azide undergoes a bond migration to form an isocyanate. Use the reaction below and a "curved-arrow" mechanism to show how this happens. (**5 points**)



b. Jeff Aube' and coworkers commonly take advantage of a similar reaction (the Schmidt rearrangement) to make bicyclic alkaloids. The reaction (illustrated below) works because the ring amine in the key intermediate can invert an place the N_2-leaving group in an equatorial position. Use an orbital picture to explain why the N_2-leaving group needs to be equatorial for the reaction to work well. (**5 points**)

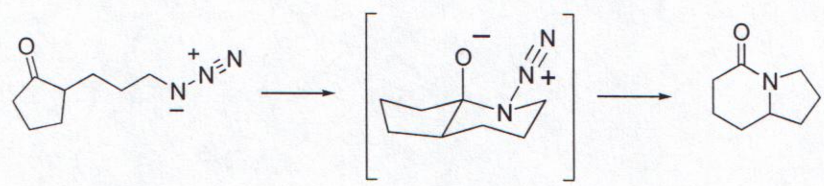


TABLE 11-4

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%	^{15}N 0.4%	
oxygen	^{16}O 99.8%		^{18}O 0.2%
sulfur	^{32}S 95.0%	^{33}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	^{127}I 100.0%		

Periodic Table of the Elements

			1 H 1.008														2 He 4.003
3 Li 6.94	4 Be 9.01											5 B 10.81	6 C 12.011	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18
11 Na 22.99	12 Mg 24.31											13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.06	17 Cl 35.45	18 Ar 39.95
19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.90	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.71	29 Cu 63.55	30 Zn 65.37	31 Ga 69.72	32 Ge 72.59	33 As 74.92	34 Se 78.96	35 Br 79.90	36 Kr 83.80
37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.94	43 Tc 98.91	44 Ru 101.07	45 Rh 102.91	46 Pd 106.4	47 Ag 107.87	48 Cd 112.40	49 In 114.82	50 Sn 118.69	51 Sb 121.75	52 Te 127.60	53 I 126.90	54 Xe 131.30
55 Cs 132.91	56 Ba 137.34	57 La 138.91	72 Hf 178.49	73 Ta 180.95	74 W 183.85	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.09	79 Au 196.97	80 Hg 200.59	81 Tl 204.37	82 Pb 207.19	83 Bi 208.98	84 Po (209)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra 226.03	89 Ac (227)	104 (Rf) (261)	105 (Ha) (262)	106 (263)												

Lanthanides	58 Ce 140.12	59 Pr 140.91	60 Nd 144.24	61 Pm (145)	62 Sm 150.35	63 Eu 151.96	64 Gd 157.25	65 Tb 158.93	66 Dy 162.50	67 Ho 164.93	68 Er 167.26	69 Tm 168.93	70 Yb 173.04	71 Lu 174.97
Actinides	90 Th 232.04	91 Pa (231)	92 U 238.03	93 Np (237)	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (249)	98 Cf (249)	99 Es (254)	100 Fm (257)	101 Md (258)	102 No (259)	103 Lr (260)

Numbers in parentheses: available radioactive isotope of longest half-life.