Name: _____

CHEM 322. Midterm 3

Spring 2011

Prof Donald Watson, Prof Mary Watson

Please write your answers clearly in the boxes provided. If your answer is illegible or outside the box, it will not be graded. You may use the back of test pages for scratch work.

You may use molecular models.

Use of calculators, cell phones, headphones, or any other electronic device during this exam is prohibited.

No notes or books may be used during this exam. Data tables are provided on pages 9 and 10 of this exam.

You may raise your hand to ask a question if you are not sure what is being asked of you.

There are 12 pages in this exam. Please check that your test has 12 pages before you begin. The last 2 pages are blank and may be used as scratch paper.

Please circle your lab section:

Mon 12:20–3:20 (Amber, 031)
Mon 3:35–6:35 (Tatsiana, 032)
Mon 7–10 (Craig, 033)
Tues 9:30–12:30 (Srimoyee, 020)
Tues 12:30–3:30 (Neo, 021)
Tues 3:30–6:30 (Peter, 022)
Tues 7–10 (Peter, 023)
Wed 12:20–3:20 (Tatsiana, 034)
Wed 7–10 (Tatsiana, 035)
Thurs 9:30–12:30 (Srimoyee, 024)
Thurs 12:30–3:30 (Neo, 026)
Thurs 3:35–6:35 (Srimoyee, 027)
Thurs 7–10 (Neo, 030)
Fri 9:05–12:05 (Amber, 036)
Fri 12:20–3:20 (Amber, 028)
Fri 3:35–6:35 (Jesse, 025)
Fri 7–10 (Jesse, 039)

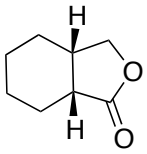
Question	Points	
1	_____	/5
2	_____	/9
3	_____	/12
4	_____	/10
5	_____	/24
6	_____	/18
7	_____	/8
8	_____	/7
9	_____	/7
Total	_____	/100

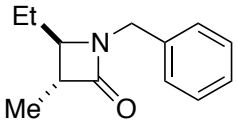
Name: _____

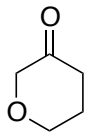
1) (5 Points) In the space below, draw *N*-methyl-4-phenyl-2-azacyclohexanone.

2) (9 Points) For each of the following, which term bests described the molecule? Please write the appropriate letter in the box below each structure.

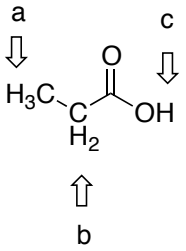
A) δ-lactone B) ketone C) δ-lactam D) β-lactam E) γ-lactone

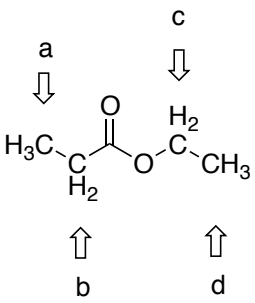


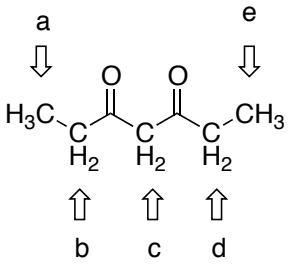




3) (12 Points) In the boxes below, please give the letter of the most acidic protons in each of the following molecules.

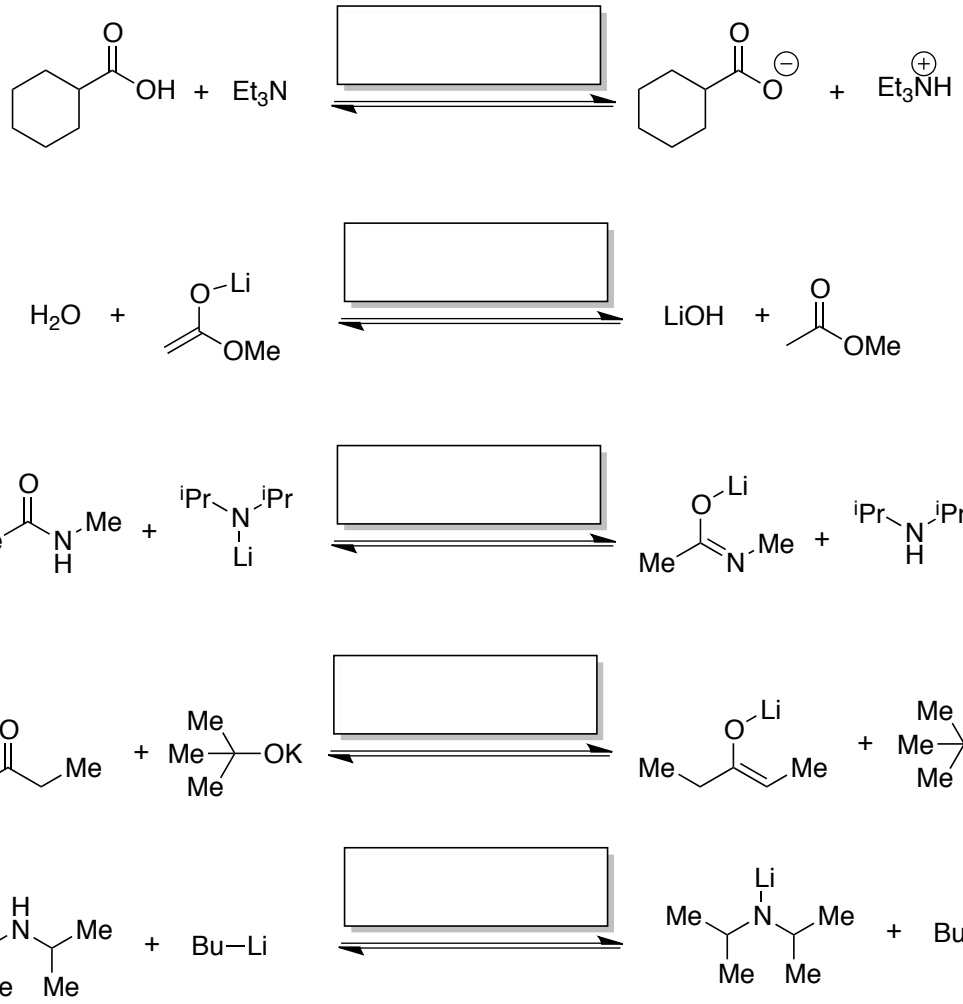






Name: _____

4) (10 Points) For each of the follow reactions, please predict the equilibrium position by indicating if the reaction is strongly endothermic, strongly exothermic or approximately thermoneutral. Write “endothermic”, “exothermic” or “neutral” in the boxes.



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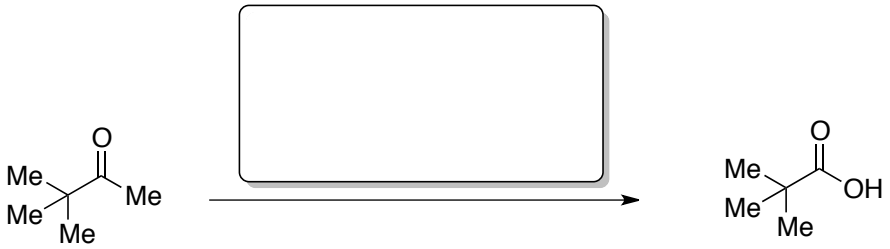
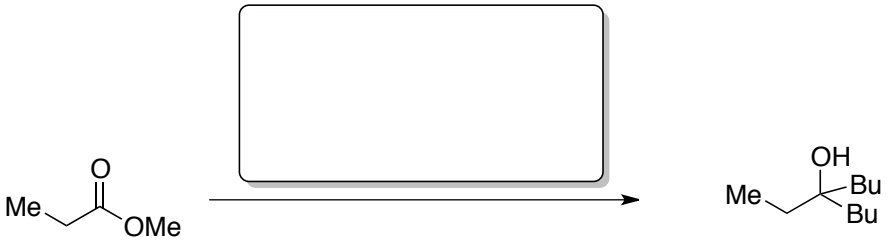
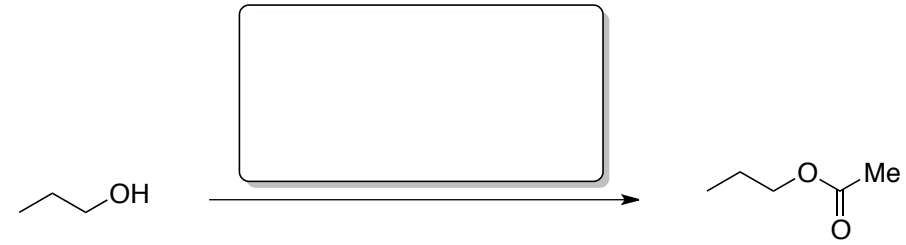
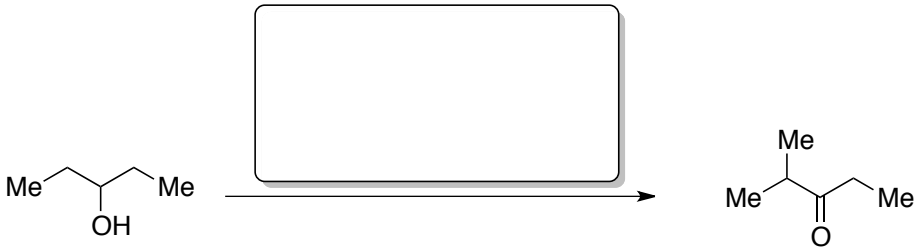
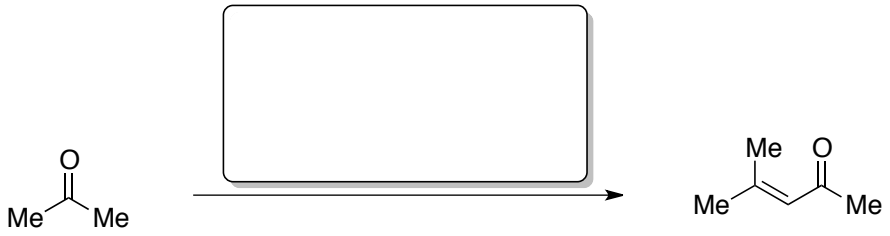
5) (24 Points) Please provide the necessary reagents to complete the following transformations.

(a) 

(b) 

(c) 

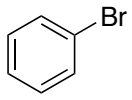
(d) 

(e) 

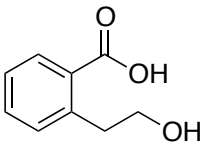
(f) 

Name: _____

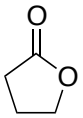
6) (18 Points) Please predict the product of the following reactions. If no reaction is expected, state "No Reaction".

(a) 

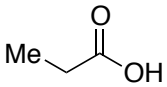
1) Mg
2) CO_2
3) MeOH, HCl, heat

(b) 

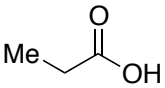
HCl, heat

(c) 

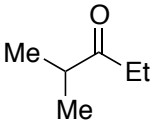
1) $LiAlH_4$ (excess)
2) H_3O^+

(d) 

DCC, Me_2NH

(e) 

NaH; then MeI

(f) 

LDA, –78 °C;
then MeI

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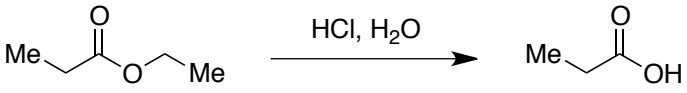
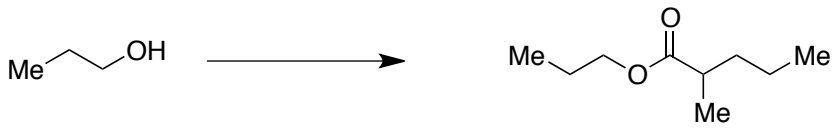
7) (8 Points) Please provide a reasonable arrow-pushing mechanism for the following reaction.



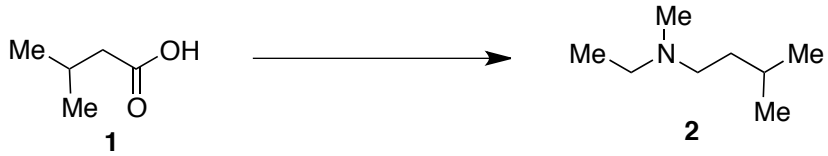
Name: _____

8) (7 points) Using 1-propanol as your only source of carbons, provide a synthesis of propyl 2-methylpentanoate. You may use any inorganic reagents.



Name: _____

9) (7 Points) Please suggest a synthesis of amine **2** starting from acid **1** and any other reagents you need that contain two (2) or less carbons.



1 **2**

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Approximate IR Absorption Frequencies

Bond	Frequency (cm^{-1})	Intensity
O–H (alcohol)	3650–3200	Strong, broad
O–H (carboxylic acid)	3300–2500	Strong, very broad
N–H	3500–3300	Medium, broad
C–H	3300–2700	Medium
C≡N	2260–2220	Medium
C≡C	2260–2100	Medium to weak
C=O	1780–1650	Strong
C–O	1250–1050	Strong

Approximate ^{1}H NMR Chemical Shifts

Hydrogen	δ (ppm)
CH_3	0.8–1.0
CH_2	1.2–1.5
CH	1.4–1.7
C=C–CH_x	1.7–2.3
O=C–CH_x	2.0–2.7
Ph–CH_x	2.3–3.0
≡C–H	2.5
R_2N–CH_x	2.0–2.7
I–CH_x	3.2
Br–CH_x	3.4
Cl–CH_x	3.5
F–CH_x	4.4
O–CH_x	3.2–3.8
C=CH	4.5–7.5
Ar–H	6.8–8.5
O=CH	9.0–10.0
ROH	1.0–5.5
ArOH	4.0–12.0
RNH_x	0.5–5.0
$CONH_x$	5.0–10.0
RCOOH	10–13

Approximate ^{13}C NMR Chemical Shifts

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

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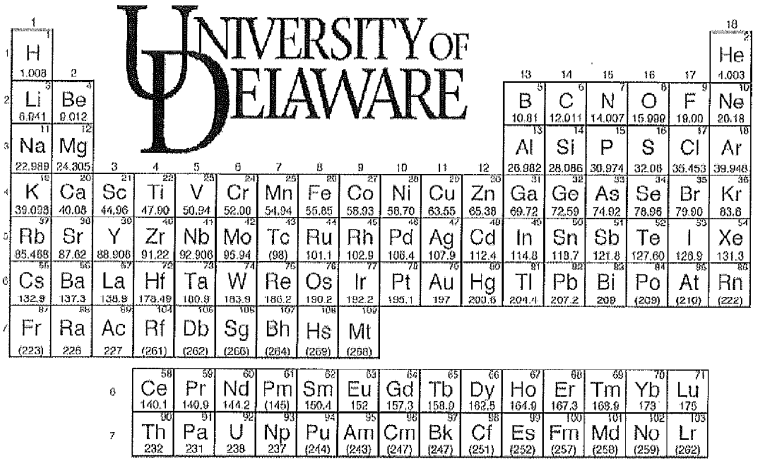
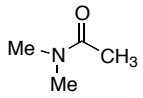
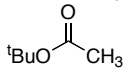
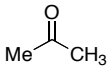
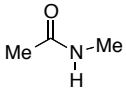
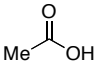


pKa TABLE

compound	pKa
Bu-H	48
Ph-H	43
H_2	~36
iPr_2N-H	~35
 (amide α-H)	25
 (ester)	24
 (ketone)	17-20
 (amide N-H)	~18
iPrOH	16-18
H_2O	16
Et_3N-H$^+$	10
 (carboxylic acid)	-1-6
H_3O^+	–2
HCl	–8

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