Chemistry 3B, Midterm 2

Wednesday, November 13, 2002

Student name: Answer Key

Student signature: _____

Write TA's name or Lecture Only: _____

1. Please make sure that the exam has 9 pages including this one.
2. Please write your answers in the spaces provided.
3. Write clearly; illegible or ambiguous answers will be considered incorrect.
4. Only writing implements are allowed **(No Calculators)**.

GOOD LUCK!

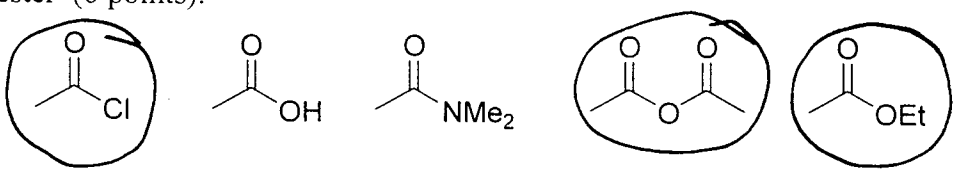
1.	30 points	_____
2.	60 points	_____
3.	20 points	_____
4.	20 points	_____
5.	20 points	_____
6.	20 points	_____
7.	10 points	_____
Total	**180 points**	_____

MINI-PERIODIC TABLE

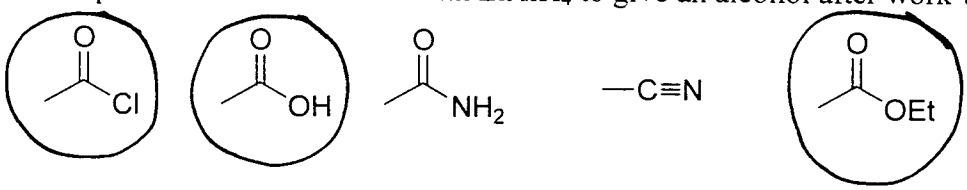
I	II	III	IV	V	VI	VII	VIII
H							He
Li	Be	B	C	N	O	F	Ne
Na	Mg	Al	Si	P	S	Cl	Ar
K	Ca	Ga	Ge	As	Se	Br	Kr

1. Answer the following questions. Every wrong answer cancels a correct answer (30 points).

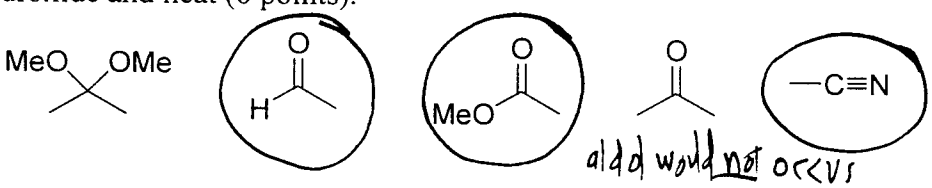
(a). Circle the carboxylic acid derivatives that upon heating with methoxide in methanol provide the methyl ester (6 points).



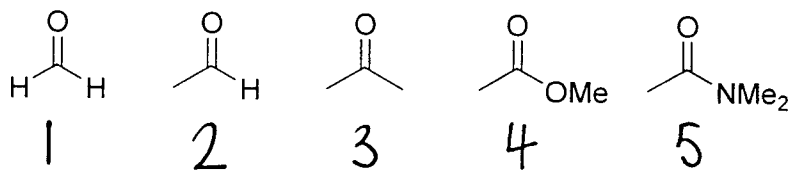
(b). Circle the compounds that would react with $LiAlH_4$ to give an alcohol after work-up (6 points).



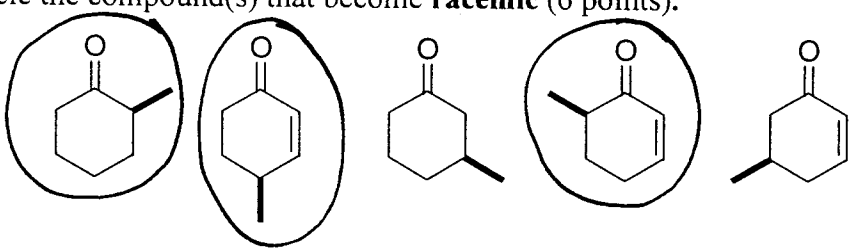
(c). Circle the compounds that are converted into a **new** compound upon treatment with aqueous sodium hydroxide and heat (6 points).



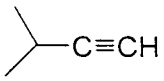
(d). Rank the following carbonyl compounds from most electrophilic to least electrophilic [1 = **most** electrophilic, 5 = **least** electrophilic] (6 points).



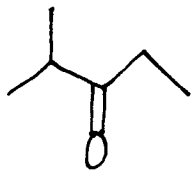
(e). Each of these enantiomerically pure compounds is heated with H_2O, H^+ for an extended period of time. Circle the compound(s) that become **racemic** (6 points).

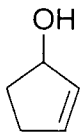


2. For each of the following reactions supply the missing reagents or major organic product in the space provided. If no reaction is expected indicate by N.R. (60 points total).

(a) 

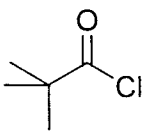
1. H_2O, H^+, Hg^{2+}
2. LDA
3. MeI

→ 

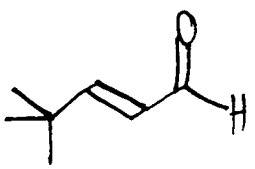
(b) 

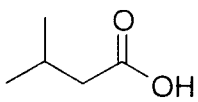
1. MnO_2
2. EtMgBr
3. aqueous workup

→ 

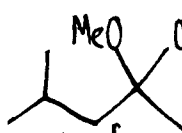
(c) 

1. $LiHAl[OC(CH_3)_3]_3$
2.  , HO-, Δ

→ 

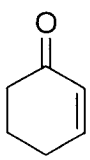
(d) 

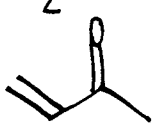
1. $SOCl_2$
2. Et_2CuLi
3. MeOH, H+

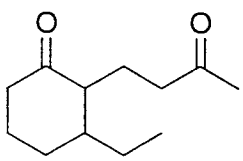
→ 

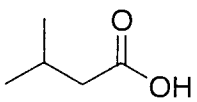
Should have had sieves

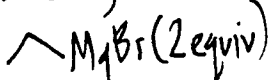
full credit for ketone or hemiacetal

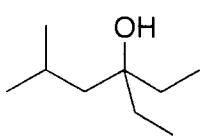
(e) 

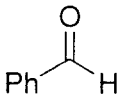
1. Et_2CuLi
2. 

→ 

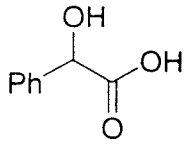
(f) 

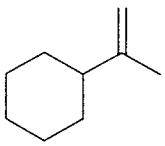
1. MeOH, H⊕
2. 
3. H_2O, H⊕

→ 

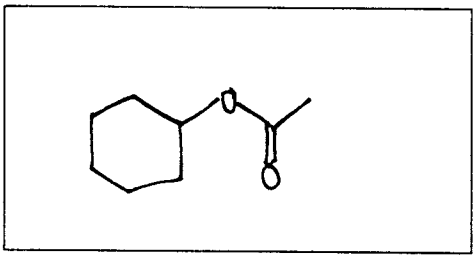
(g) 

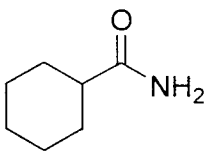
1. HCN
2. $H^{\oplus}$, H_2O, Δ

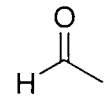


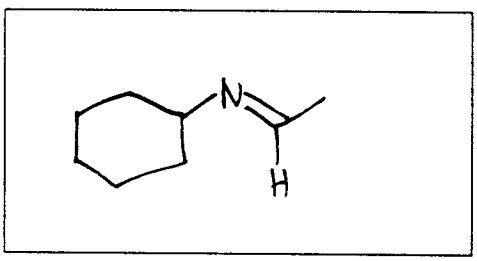
(h) 

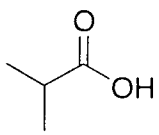
1. O_3
2. Zn, AcOH
3. CF_3CO_3H



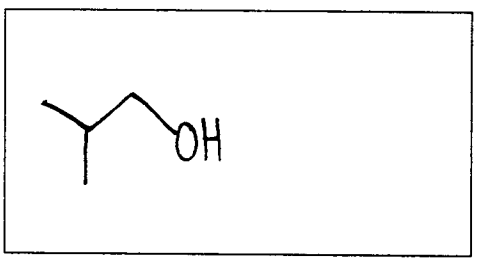
(i) 

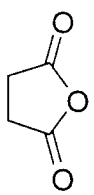
1. Cl_2, NaOH, H_2O
2.  , sieves



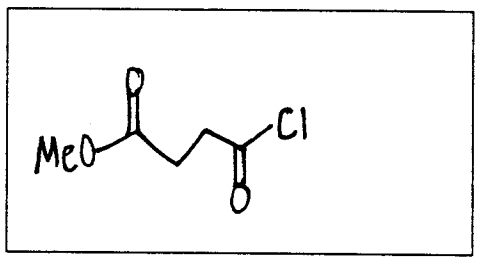
(j) 

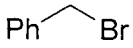
1. CH_2N_2
2. $LiAlH_4$
3. aqueous work-up



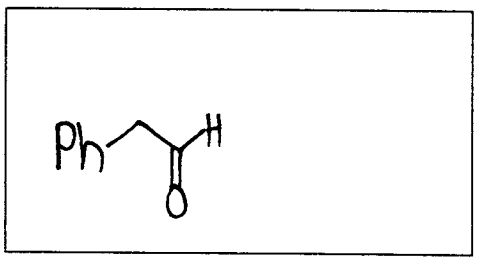
(k) 

1. MeOH
2. $SOCl_2$

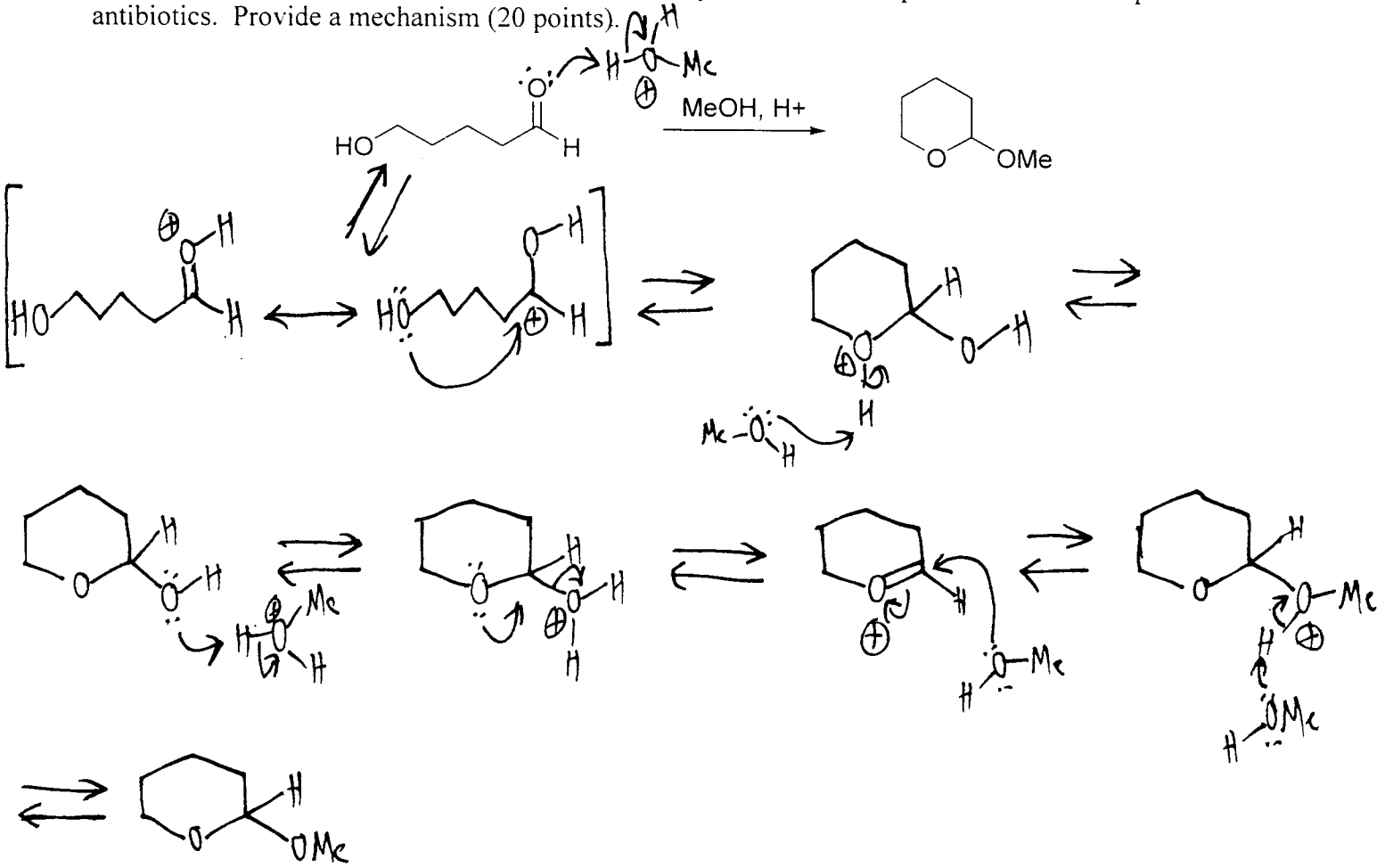


(l) 

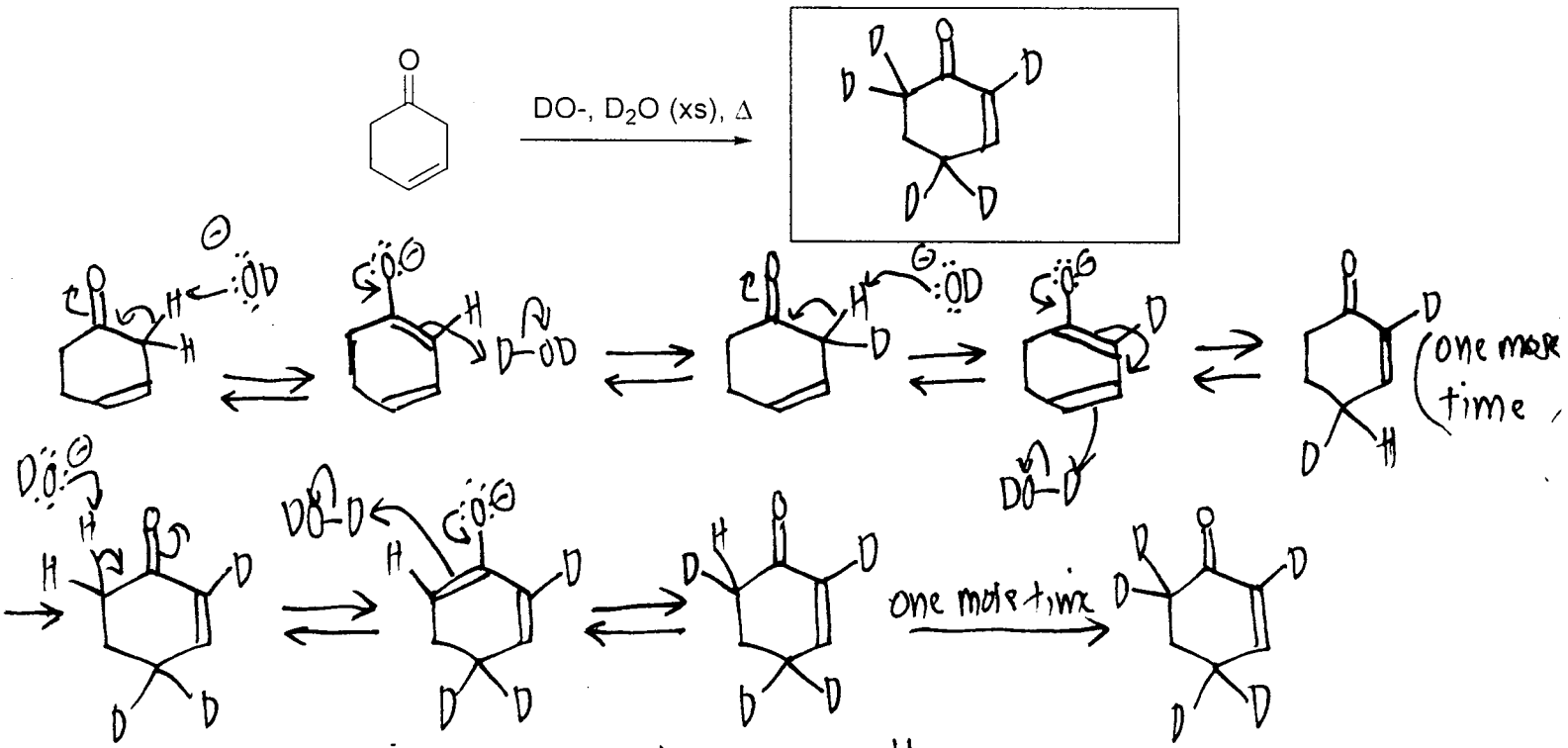
1. NaCN
2. $HAl[CH_2CH(CH_3)_2]_2$



3. The following reaction is extensively used in the synthesis of the important class of ionophore antibiotics. Provide a mechanism (20 points).

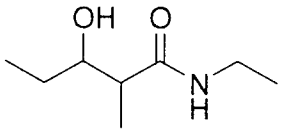


4. Draw the product of the below transformation and show the mechanism for its formation. Make sure to provide a mechanism for all sites of deuterium incorporation (20 points).

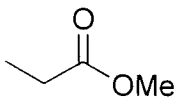


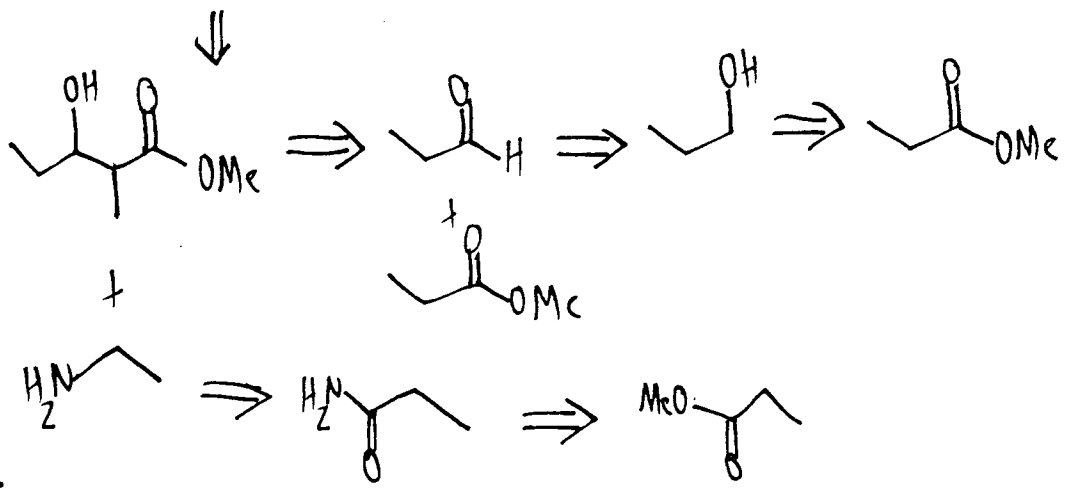
Any order of deuterium incorporation is acceptable

5. Provide the most efficient synthesis. You may employ any reagents of your choice (20 points).

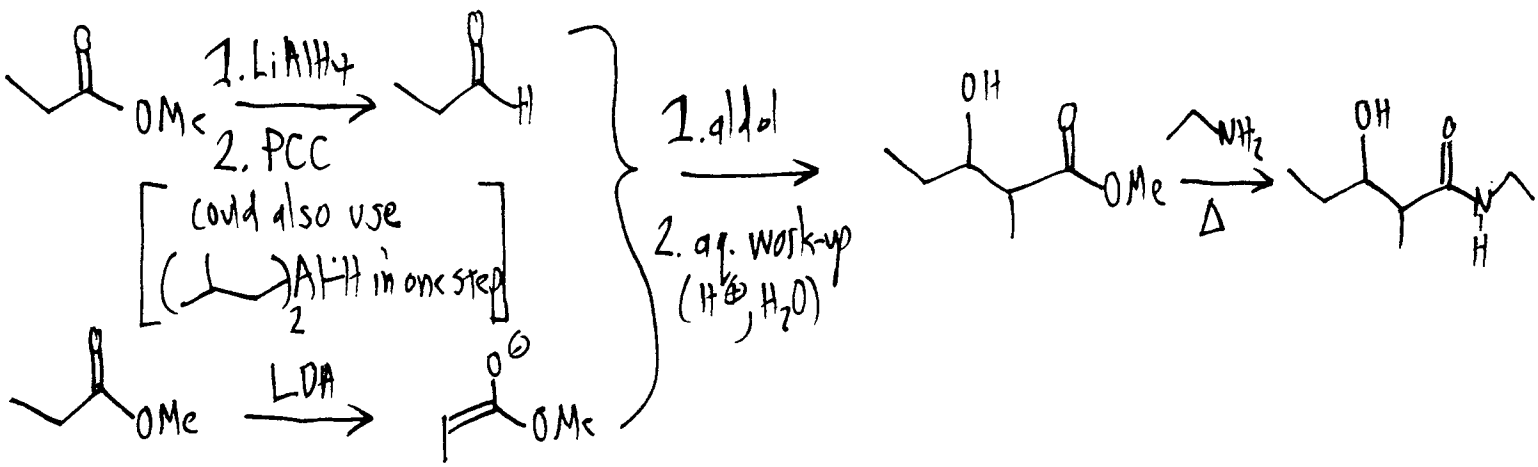


from 3 equiv of

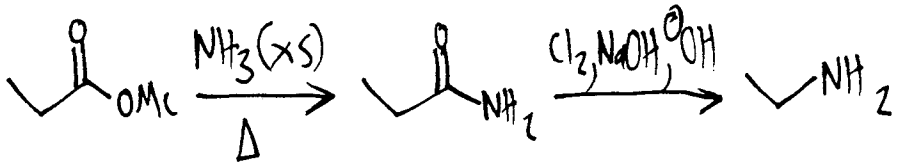




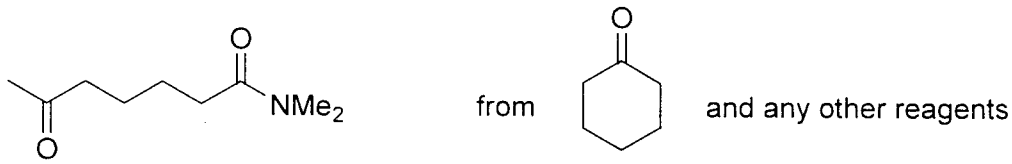
Synthetic direction

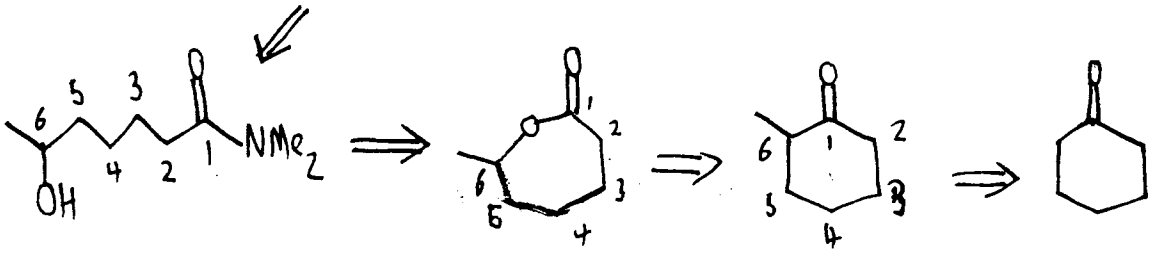


amine preparation

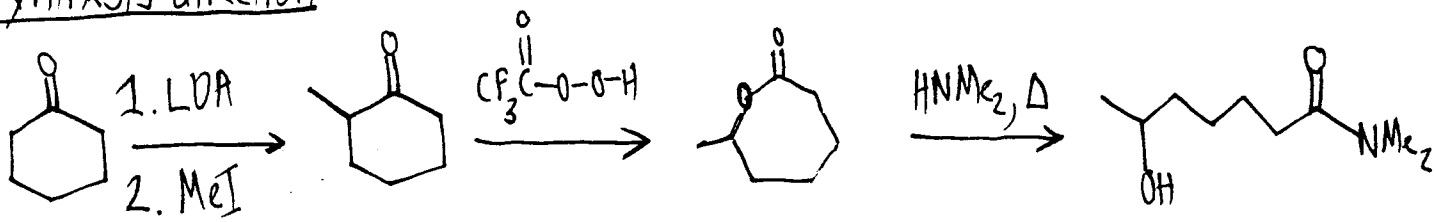


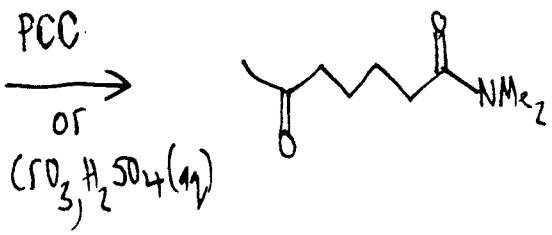
6. Provide the most efficient synthesis. You may employ any reagents of your choice (20 points).





Synthesis direction

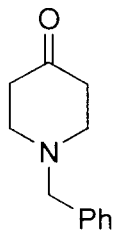


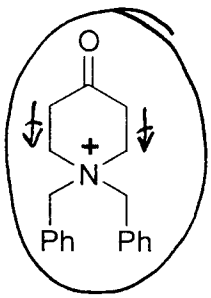


A couple of other routes were also assigned full credit

7.

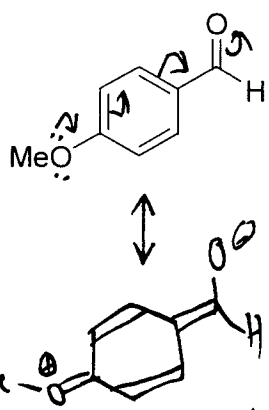
(a) The molecules drawn below are key building blocks in the synthesis of many psychoactive drugs. Circle the compound that would have the **largest** K_{eq} for hydrate formation. **Provide a brief explanation for your answer.** (5 points).



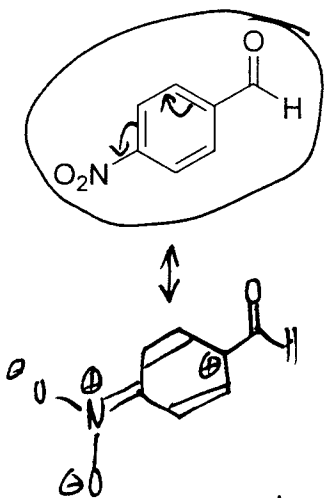


The positively charged withdraws e^{θ} density inductively thereby destabilizing the carbonyl

(b) Circle compound below that would have the **largest** Keq for hydrate formation. **Provide a brief explanation for your answer.** (5 points).



carbonyl stabilized by resonance



resonance into nitro group destabilizes carbonyl

Chemistry 3B, Practice Midterm 1

Thursday, November 7, 2002

Student name: Answer Key

Student signature: _____

Write TA's name or Lecture Only: _____

1. Please make sure that the exam has 9 pages including this one.
2. Please write your answers in the spaces provided.
3. Write clearly; illegible or ambiguous answers will be considered incorrect.
4. Only writing implements are allowed **(No Calculators)**.

GOOD LUCK!

1.	30 points	_____
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3.	20 points	_____
4.	20 points	_____
5.	20 points	_____
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7.	10 points	_____
Total	**180 points**	_____

MINI-PERIODIC TABLE

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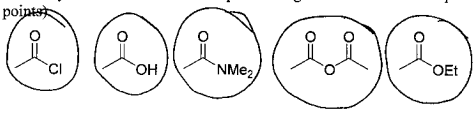
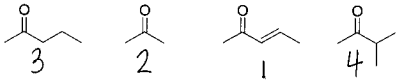
Li	Be	B	C	N	O	F	Ne
Na	Mg	Al	Si	P	S	Cl	Ar
K	Ca	Ga	Ge	As	Se	Br	Kr

1. Answer the following questions. Every wrong answer cancels a correct answer (30 points total).

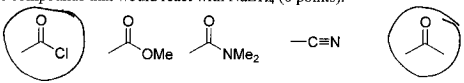
(a). Circle the carboxylic acid derivatives that upon heating with acidic methanol provide the methyl ester (6 points).



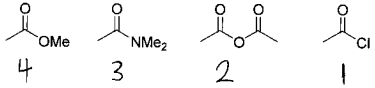
(b). Rank the structures according to the number of deuteriums incorporated upon treatment with DO-, D_2O [1 = **most** deuteriums, 4 = **fewest** deuteriums] (6 points).



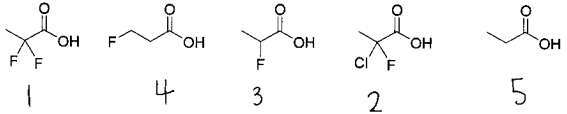
(c). Circle the compounds that would react with $NaBH_4$ (6 points).



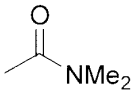
(d). Rank the compounds according to those that would react most rapidly with $LiAlH_4$ to those that would react the least rapidly [1 = **most** rapid, 4 = **least** rapid] (6 points).



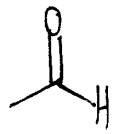
(e). Rank the following carbonyl compounds from most acidic to least acidic [1 = **most** acidic, 5 = **least** acidic] (6 points).

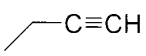


2. For each of the following reactions supply the missing reagents or major organic product in the space provided. If no reaction is expected indicate by N.R. (60 points total).

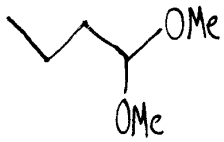
(a) 

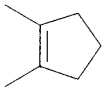
1. NaOMe, MeOH, Δ
2. $HAl[CH_2CH(CH_3)_2]_2$

→ 

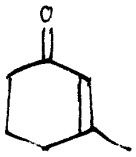
(b) 

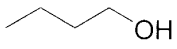
1. B_2H_6
2. H_2O_2, NaOH
3. MeOH, H+, sieves

→ 

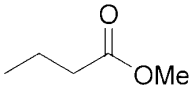
(d) 

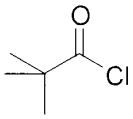
1. O_3
2. Zn, AcOH
3. NaOH, Δ

→ 

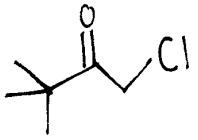
(c) 

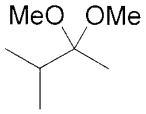
1. CrO_3, H_2SO_4, H_2O
2. MeOH, HCl

→ 

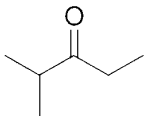
(d) 

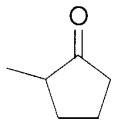
1. Me_2CuLi
2. Cl_2, AcOH

→ 

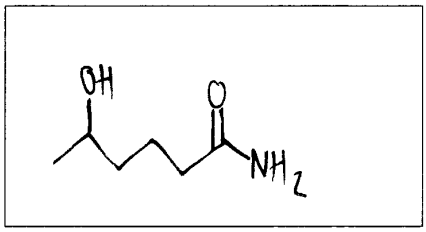
(f) 

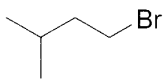
1. H_2O, HO⊖
2. LDA
3. MeI

→ 

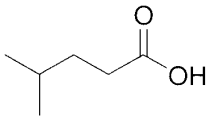
(g) 

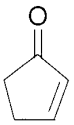
1. CF_3CO_3H
2. NH_3 (xs), Δ



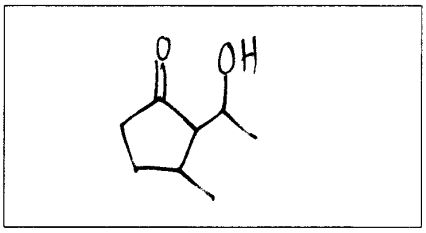
(f) 

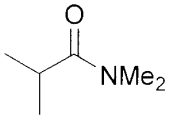
1. NaCN
2. H_2O, $H^{\oplus}$, Δ



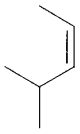
(j) 

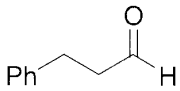
1. Me_2CuLi
2. 
3. aqueous work-up



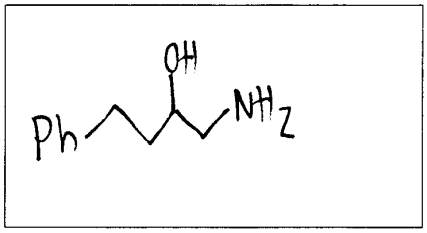
(f) 

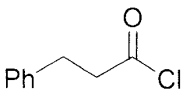
1. 
2.



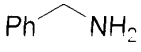
(k) 

1. HCN
2. $LiAlH_4$
3. aqueous work-up

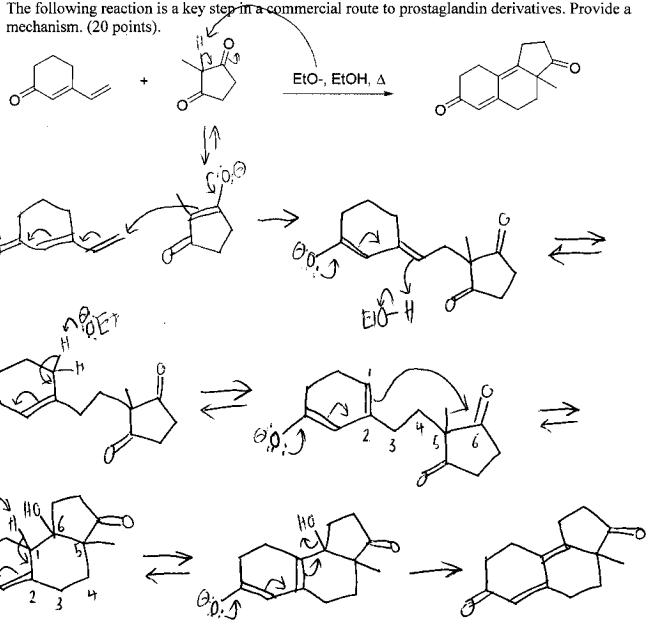


(f) 

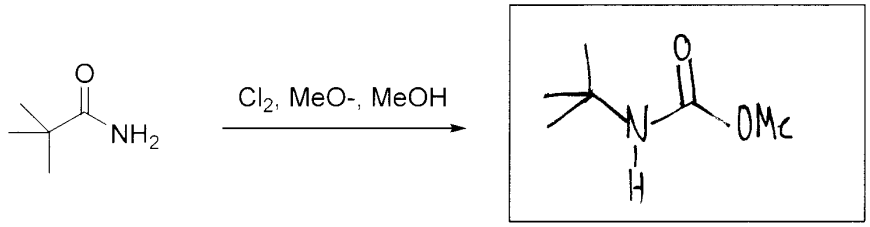
1. NH_3 ($\geq$ 2 equiv)
2. Cl_2, NaOH, H_2O

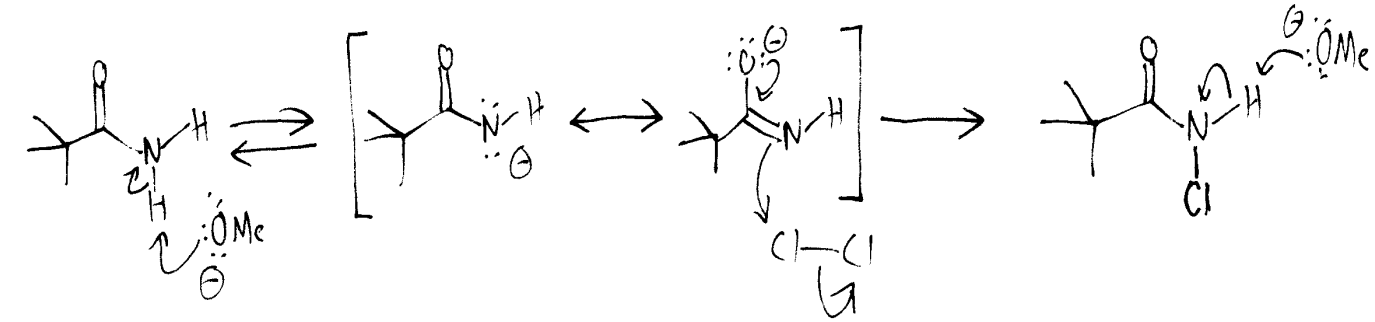


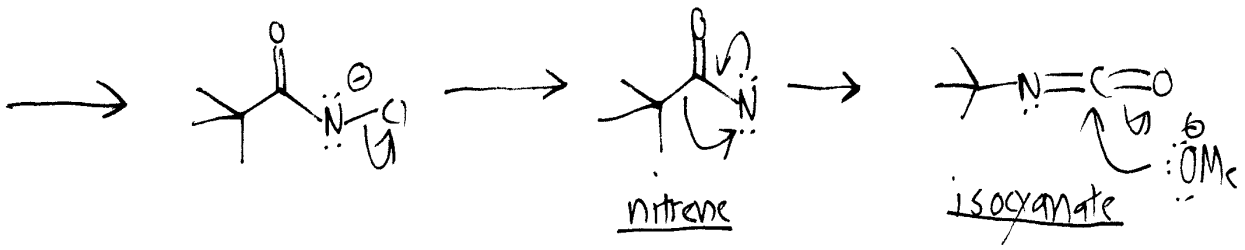
3. The following reaction is a key step in a commercial route to prostaglandin derivatives. Provide a mechanism. (20 points).

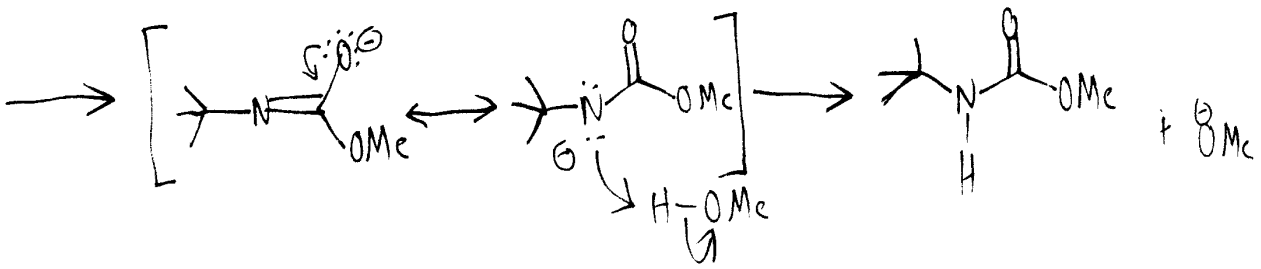


4. Draw the product of the below transformation and show the mechanism for its formation. Note that MeO-, MeOH is used in place of HO-, H_2O (20 points).

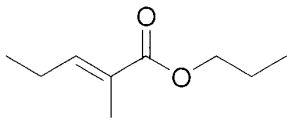


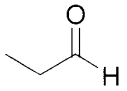




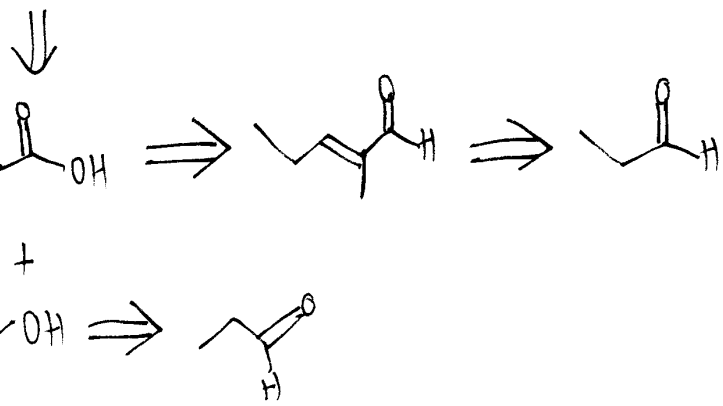


5. Provide the most efficient synthesis. You may employ any reagents of your choice (20 points).

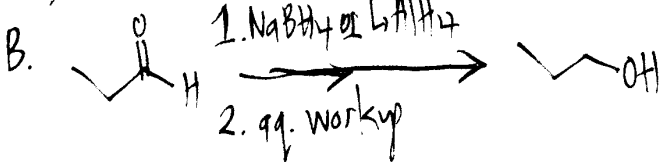


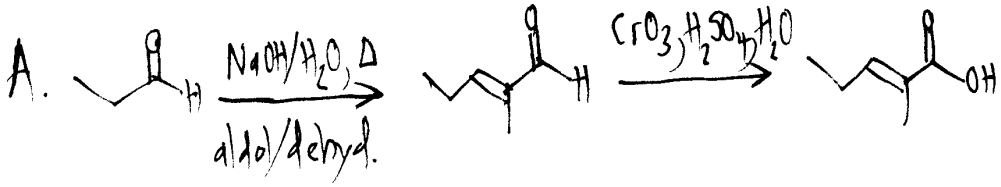
from 3 equiv of 

Retrosynthesis

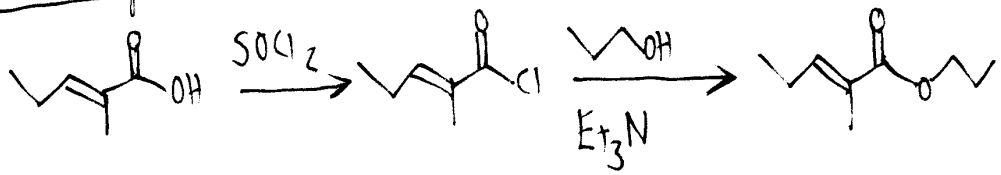


Synthetic direction

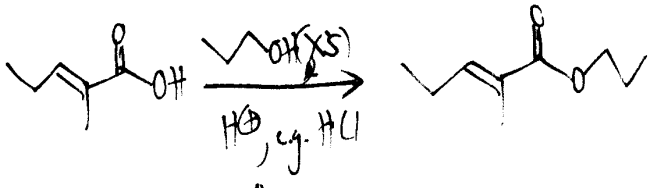




Combined pieces



Or:

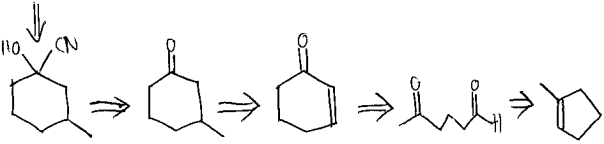


2nd method somewhat less practical since would require excess to drive rxn to completion

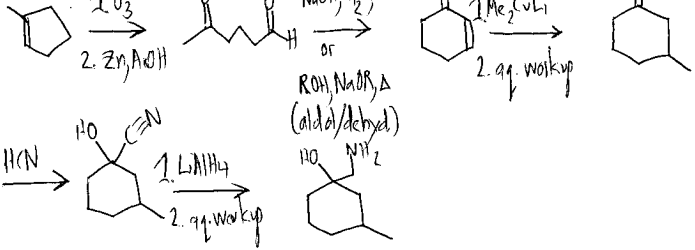
6. Provide the most efficient synthesis. You may employ any reagents of your choice (20 points).

from  and any other reagents

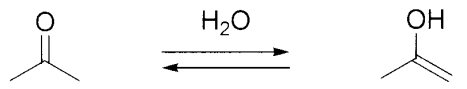
Retrosynthesis



Synthetic direction



7. Calculate the K_{eq} for the below transformation based upon the pK_a of each tautomer. Show your work (10 points).



$pK_a = 20$ $pK_a = 13$

$K_{eq} = \dfrac{[\text{enol}]}{[\text{keto}]}$

Recall that $K_a = \dfrac{[H_3O^+][A^-]}{[HA]}$, $K_a(\text{keto}) = 10^{-20} = \dfrac{[H_3O^+][\text{keto}^-]}{[\text{keto}]}$

$K_a(\text{enol}) = 10^{-13} = \dfrac{[H_3O^+][\text{enol}^-]}{[\text{enol}]}$

} terms in numerator are the same

$K_{eq} = \dfrac{K_a(\text{keto})}{K_a(\text{enol})} = \dfrac{[H_3O^+][\text{keto}^-]}{[\text{keto}]} \times \dfrac{[\text{enol}]}{[H_3O^+][\text{keto}^-]} = \dfrac{[\text{enol}]}{[\text{keto}]}$

$K_{eq} = \dfrac{10^{-20}}{10^{-13}} = 10^{-7}$

This is a difficult problem that shows the value of knowing/being able to manipulate pK_as. Based upon the emphasis of material covered in class and lack of pK_a problems I did not think it was completely appropriate for the real midterm.