Hour Exam #3
Chemistry 345
Professor Gellman
30 April 2014

Last Name Answers

First Name key

General Instructions:

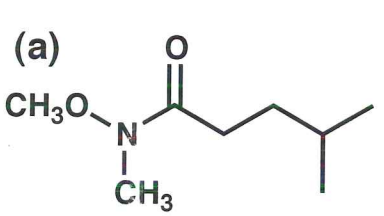
(i) Use scratch paper at back of exam to work out answers; final answers must be recorded at the proper place on the exam itself for credit. Models are allowed.

(ii) Print your name on each page.

(iii) Please keep your paper covered and your eyes on your own work. No electronic devices may be used. Misconduct will lead to failure in the course.

1. (17 points) Show the product(s) expected from the reactions indicated below.

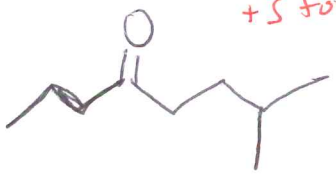
(a)



1)  Li

Et_2O

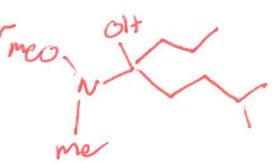
2) H_3O^+



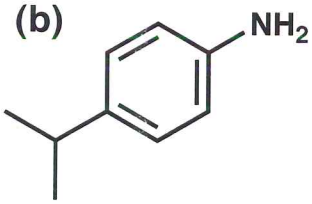
+3 for too many carbons in chain

+5

+1 for

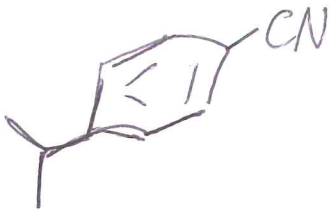


(b)



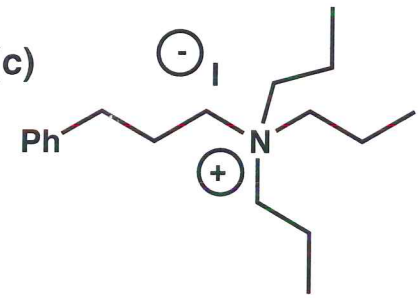
1) $NaNO_2$, H_2SO_4

2) CuCN



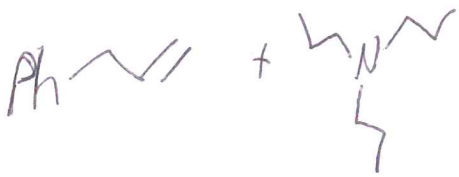
+5

(c)



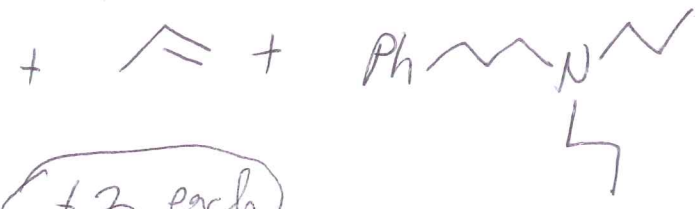
1) Ag_2O, H_2O

2) Δ



[Not required]

(+AgI + N_2O)



(+2 each)

Name _____

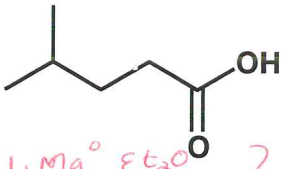
2. (21 points) Show the reagents and other organic molecules required to convert the starting material to the indicated product. Be sure to differentiate clearly between distinct steps, by using "1)", "2)", etc. over or under the arrow.

(a)

1) Mg^0, Et_2O (+3) [Li^0 ok]

2) CO_2 (+3)

3) H_3O^+ (+1)

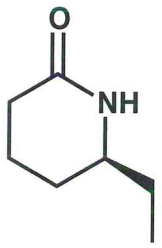


CO_2, NaOH +1

1. Mg^0 Et_2O
2. CO_2, H_3O^+ } +6

~~1) Mg^0, Et_2O~~

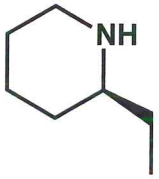
(b)



1) $LiAlH_4$ (+3)

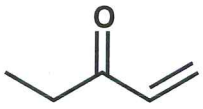
2) H_3O^+ (+1)

3) NaOH (+1)



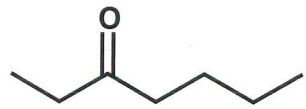
1) $LiAlH_4$
2) NaOH } +4
3) H_3O^+

(c)



1) $(CH_3CH_2)_2CuLi$ (+3)

2) H_3O^+ (+1)



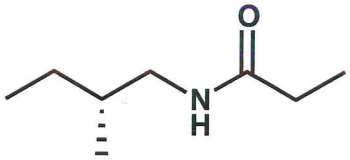
$CuLi$ +2

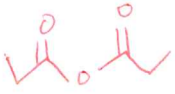
(d)

(+3)

Et_3N or pyridine

(+2)



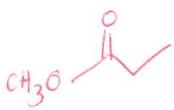


[Anhydride ok]

1) base
2) acidchloride } +2
3) acid

NaOH +0

pyridine + NaOH = +0

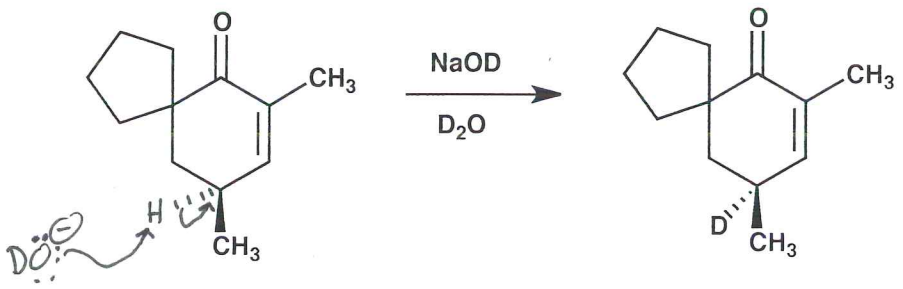


ester

+5 => slow
no base

~~without base +3~~

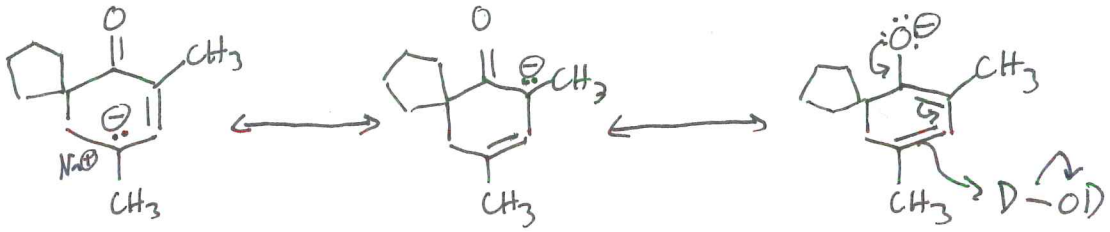
3. (19 points) Provide a mechanism (curved arrows) for each reaction shown below. Draw all important resonance structures for intermediates.



(Single enantiomer) (Racemic)

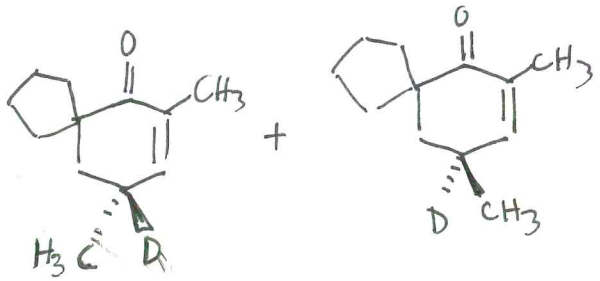
+2 for arrows

+2/+2/+1 for resonance structures (max 5)



This enolate is planar, therefore D_2O can approach from above or below, which leads to the enantiomeric products.

+2 for arrows



+9 total

-1 if no indication of both enantiomers forming

-1 for missing formal charges

-1 for incorrect use of resonance arrows

-2 for mixed acid/base (no net penalty)

0 credit for all acid mechanism

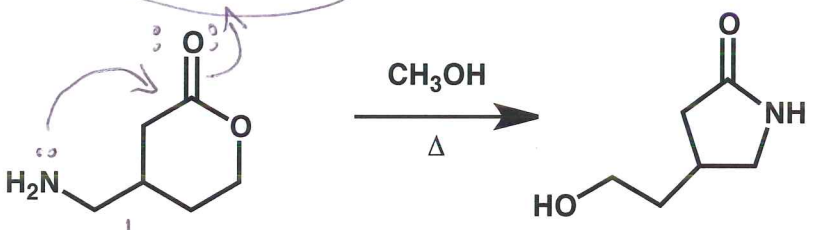
(cont. on next page)

Name _____

3. (cont.)

+2 for arrows

(b)



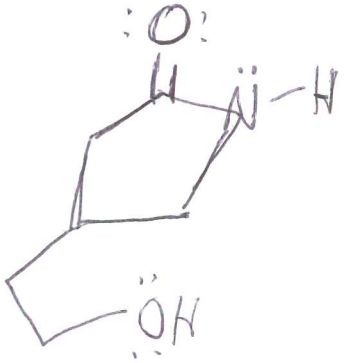
+2 for arrows

+2 for intermediate

+2 for arrows

+2 for intermediate

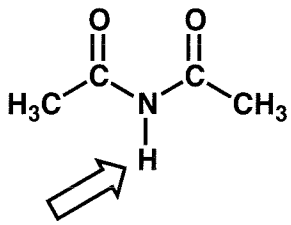
[Alternative proton transfer steps involving solvent are ok.]



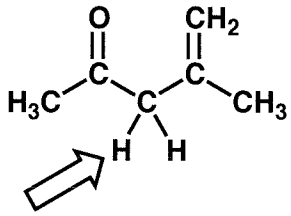
+10 total

Name _____

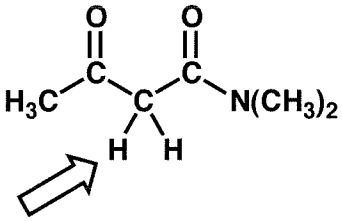
4. (8 points) Rank the four compounds below (A, B, C and D) according to pK_a at the indicated H, with the HIGHEST pK_a on the RIGHT.



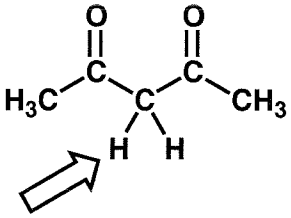
A



C



B



D

INCREASING pK_a to the RIGHT:

A < D < B < C

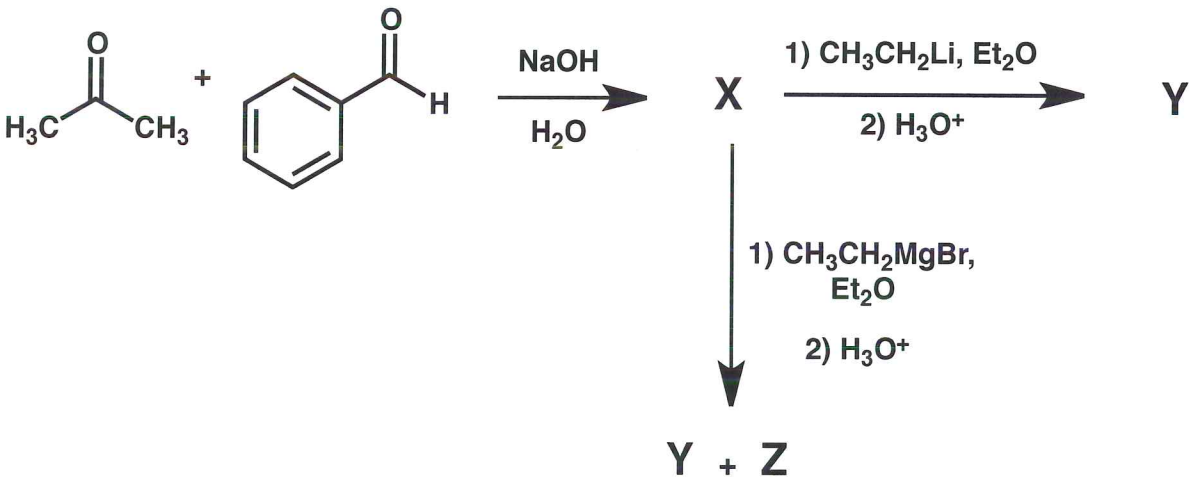
[Place the letters A, B, C and D in the blanks above, in the proper order.]

+2

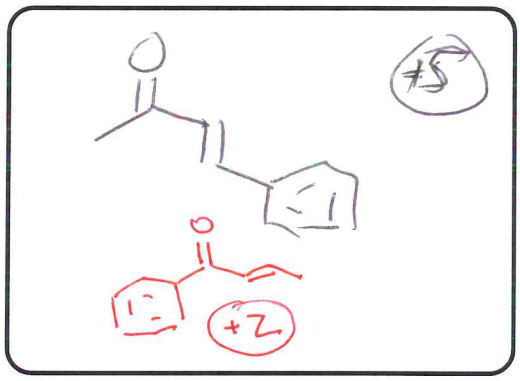
+2

Name _____

5. (15 points) Draw the structures of molecules X, Y and Z in the indicated boxes below. Your structures must be consistent with the spectroscopic data given for these compounds.



X =



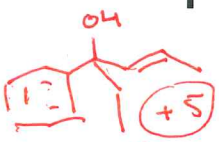
[C=C bond geometry not important]

Strong IR signal at 1680 cm^{-1}

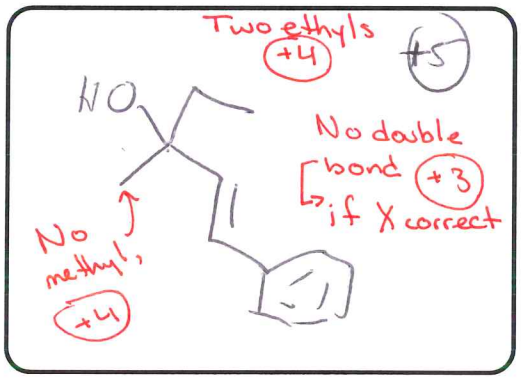
No IR signal > 3100 cm^{-1}

^{13}C NMR shows 8 resonances, only one of which is < 100 ppm.

Y =



if X is consistent

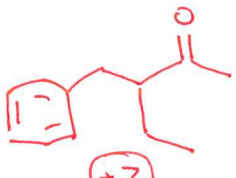


No IR signal between 1670 and 1750 cm^{-1}

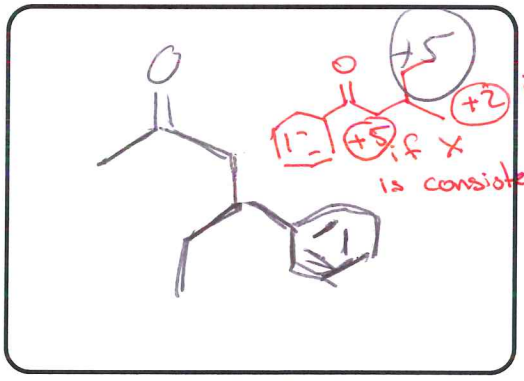
Strong IR signal at 3300 cm^{-1}

^{13}C NMR shows 10 resonances, 4 of which are < 100 ppm.

Z =



+1 for double alkylation (α, α)



if X is consistent

if α from other X structure

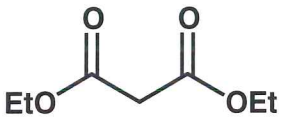
Strong IR signal at 1710 cm^{-1}

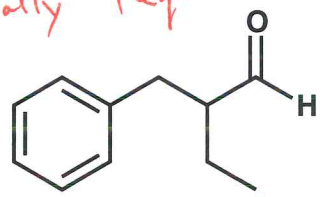
No IR signal > 3100 cm^{-1}

^{13}C NMR shows 10 resonances, 5 of which are < 100 ppm.

Name _____

6. (20 points) Propose an efficient synthetic route from the indicated starting material to the target. You may use any other starting materials and reagents.

Starting material = 

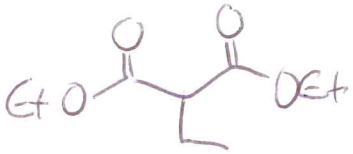
Target = 

-1 if not specifically 1 equiv

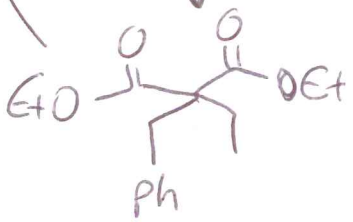
(+5) 1) 1 equiv. NaOEt, EtOH
2) CH_3CH_2Br

-1 if NaOH used

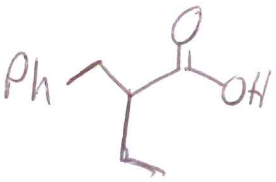
-1 for wrong # carbons



(+5) 1) 1 equiv NaOEt, EtOH
2) 



1) NaOH, H_2O
2) H_3O^+, Δ



(+6) 1) $SOCl_2$ or PCl_5
2) H_2, Poisoned catalyst ("Rosenmund")
or $LiAl(OtBu)_3H$

(+4)

Note: The "NaOEt" and "Rx" steps do not need to be separated, but the two alkylation steps do need to be separated.

-1 if steps not separated

-2 if NaOH, H_2O skipped

3/6 for $SOCl_2/PCl_5$, then wrong reductant

0 if no prefunctionalization of