Hour Exam #3
Chemistry 345
Professor Gellman
29 April 2011

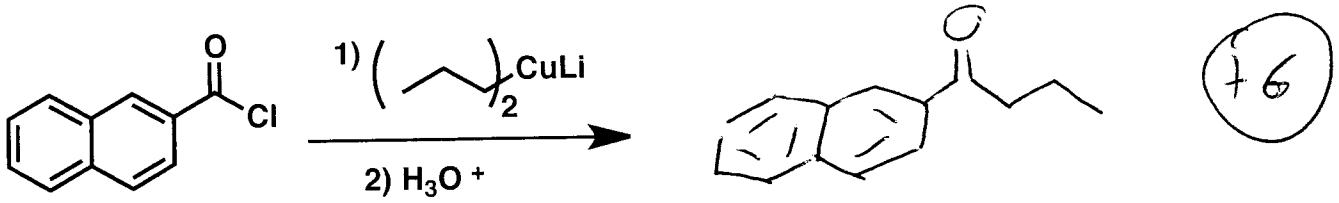
Last Name Answer

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.
(ii) Print your name on each page.

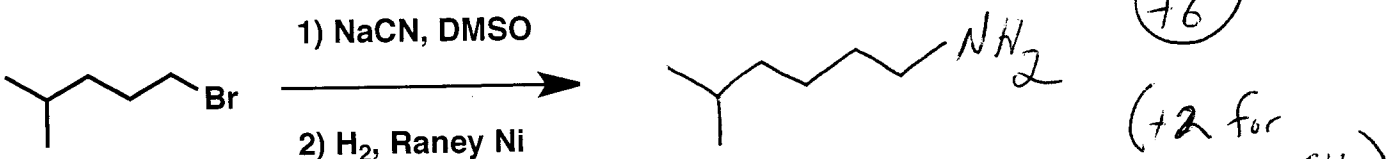
1. (20 points) Show the major product or products expected from each reaction:

(a)



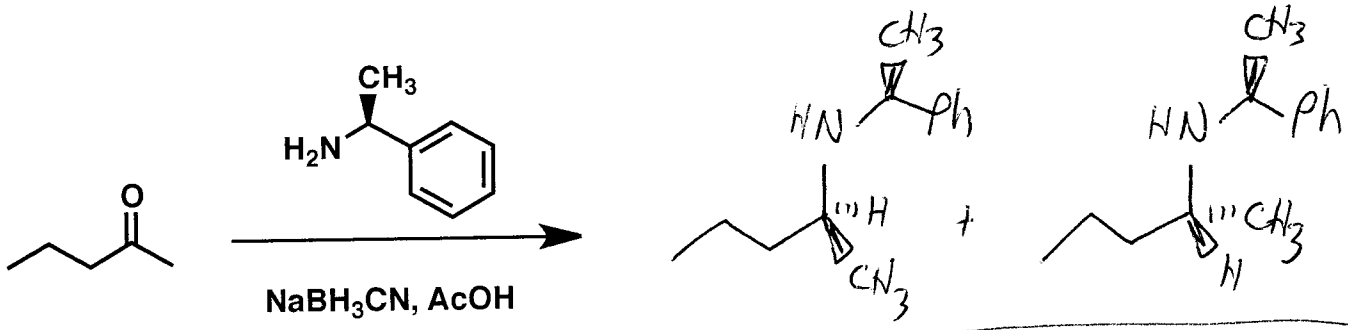
+6

(b)



+6
(+2 for missing CH_2)

(c)



[Note: The amine is a single enantiomer.]

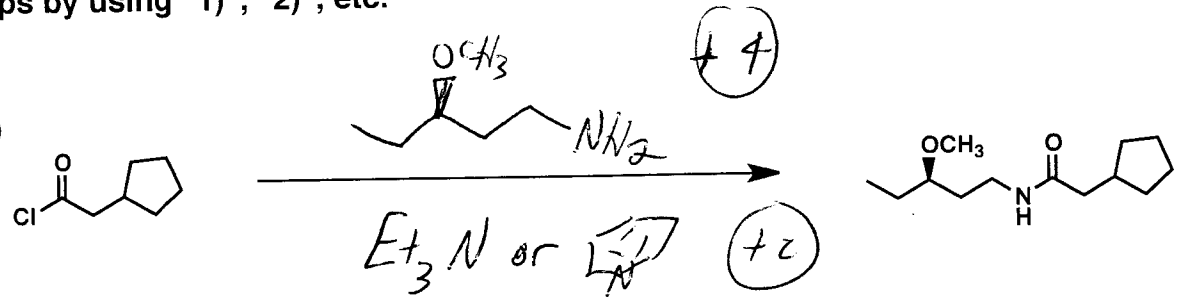
+6 for one (or no stereochem)

+8 for both

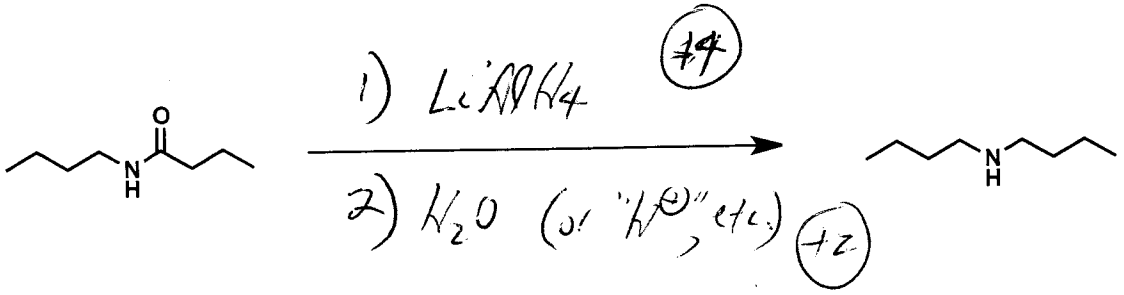
Name _____

2. (24 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.

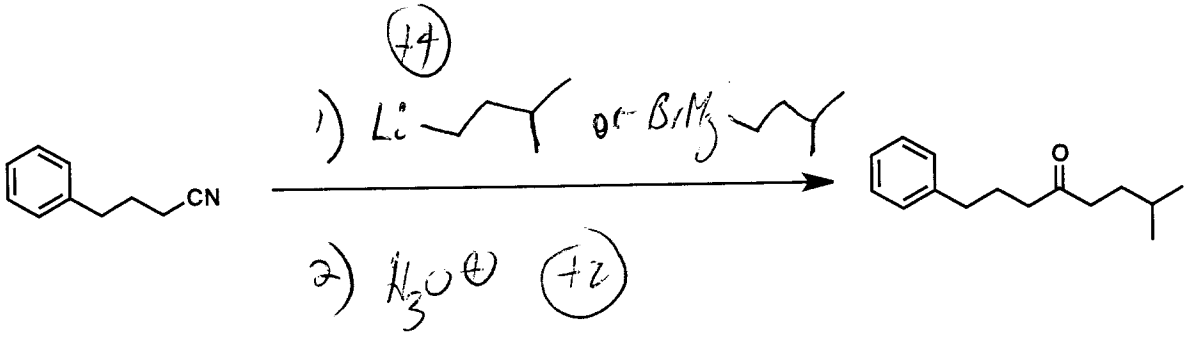
(a)



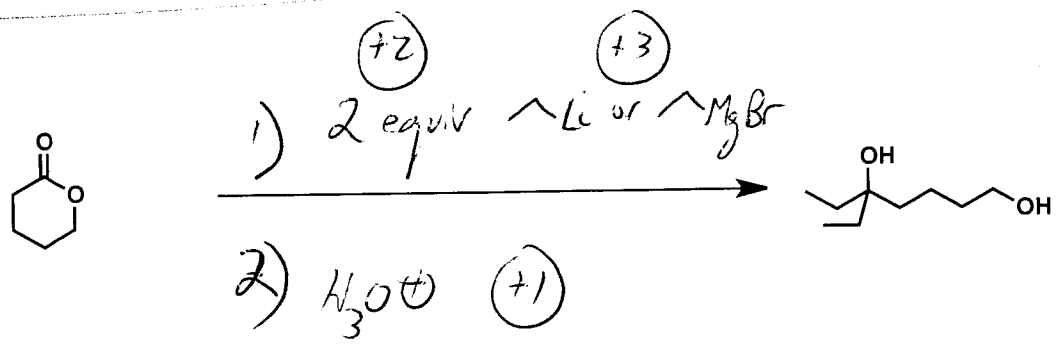
(b)



(c)



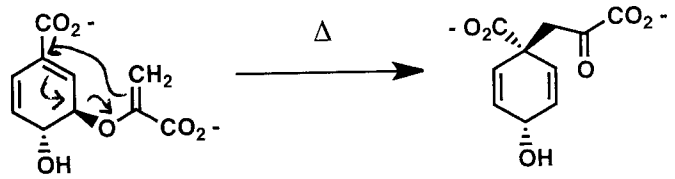
(d)



Name _____

3. (18 points) Draw out a mechanism ("curved arrows") for each reaction shown below. Be sure to show all important resonance structures in intermediates.

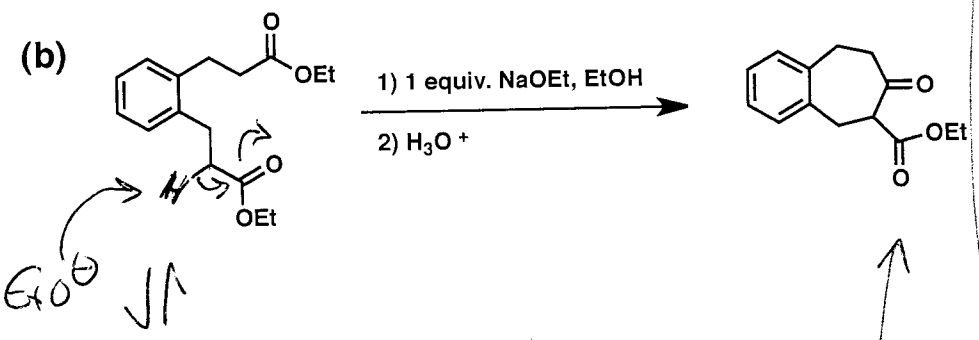
(a)



(Point of interest: This is a key step in the biosynthesis of aromatic amino acids.)

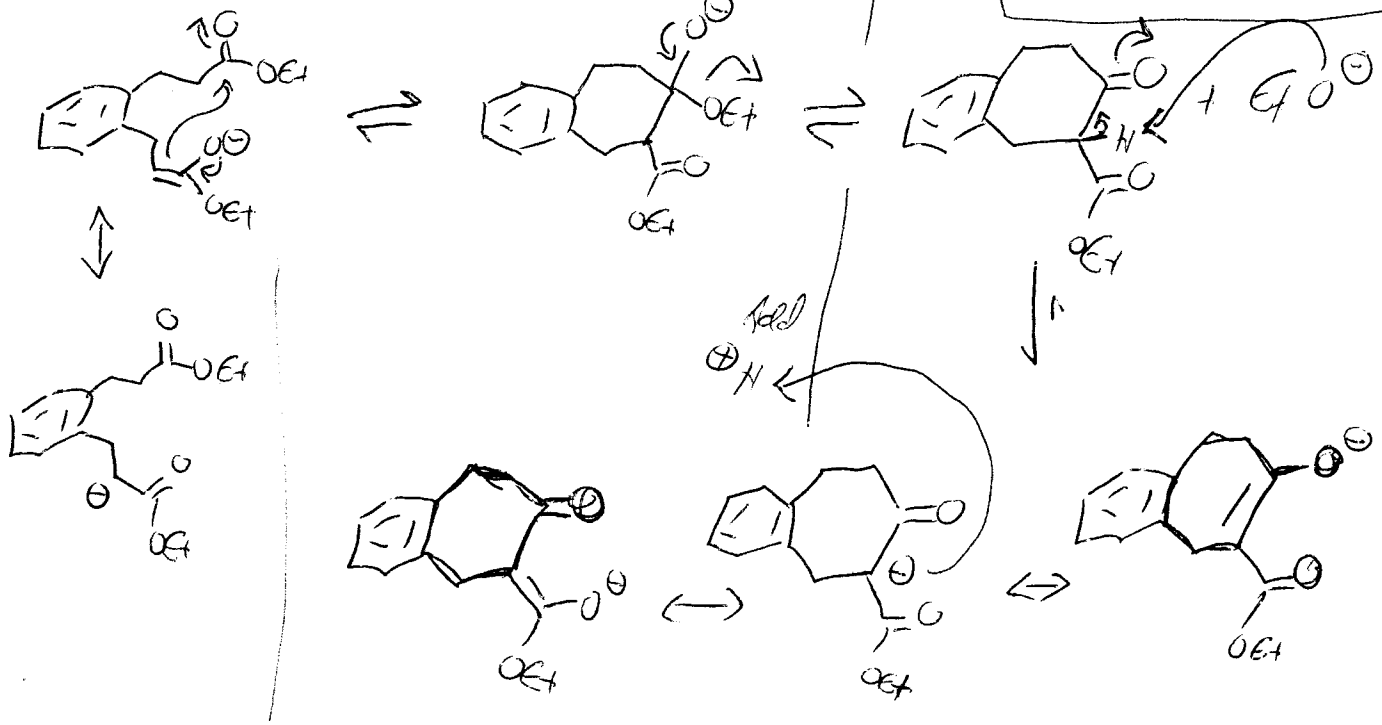
+6

(b)



+1 for each intermediate & res. structure (+7 total)

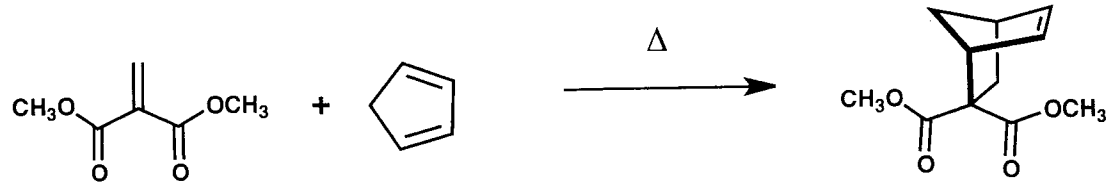
+1 for each set of arrows (+5 total)



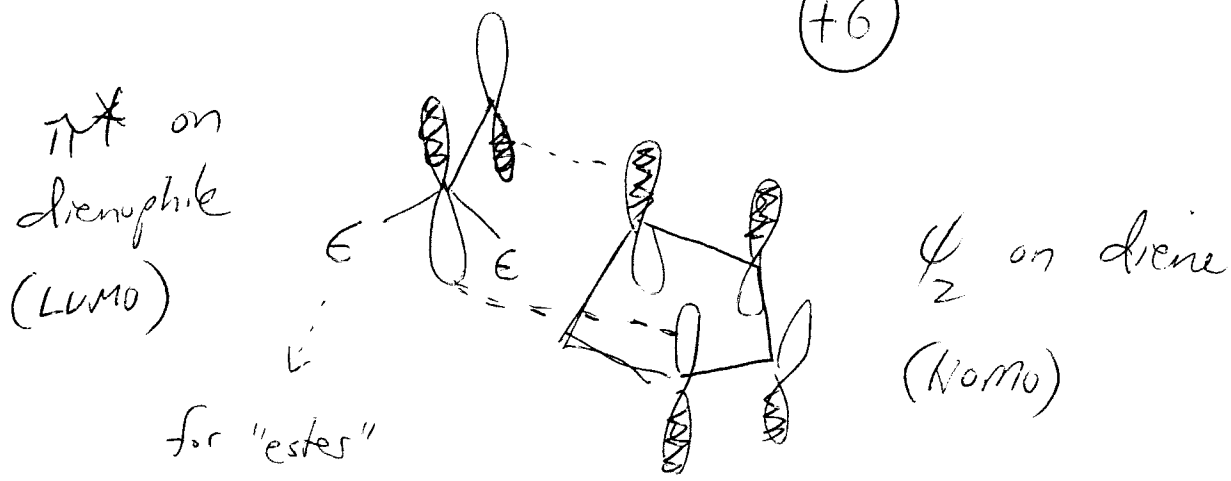
Name _____

4. (18 points)

(a) The two molecules shown below react upon gentle heating to form the indicated product. The mechanism is concerted. Provide drawings that indicate the π molecular orbital on each reactant that is involved in the reaction; your drawing should show how molecular orbital symmetry considerations are consistent with the ease with which this reaction occurs.



+6



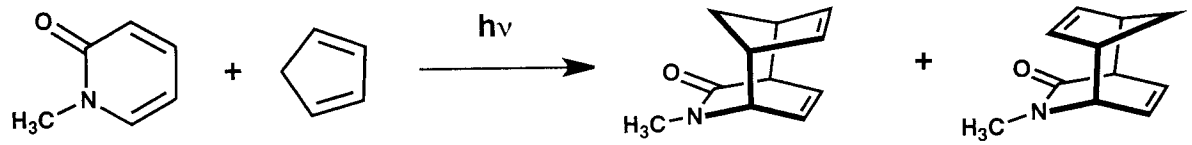
Note: OK to do HOMO on dienophile (π) + LUMO on dienophile (ψ_3).

-- cont. on next page --

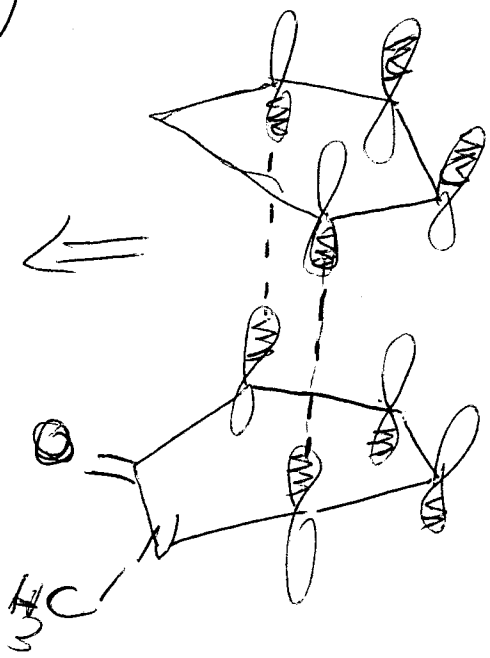
4. (cont.)

Name _____

(b) The pair of molecules shown below do not react upon heating, but they form the two isomeric products shown when exposed to light. Provide drawings that indicate the π molecular orbital on each reactant that is involved in the photo-reaction.



+6



Excited state

HOMO (ψ_3)

MO symmetry matches ⇒ allowed (photochemically)

Ground state

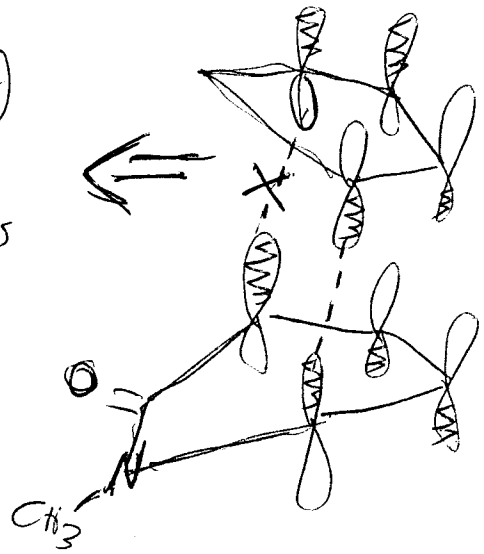
LUMO (ψ_3)

(c) For the reaction shown above (part (b)), provide a molecular orbital symmetry-based explanation for the lack of a thermal reaction.

Ground state

NOMO (ψ_2)

+6



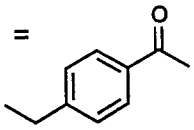
MO symmetry mismatch if both components in ground state.

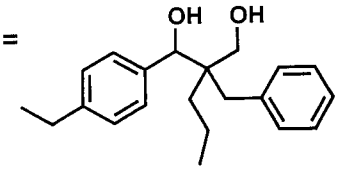
Ground state

LUMO (ψ_3)

Name _____

5. (20 points) Propose an efficient synthetic route from the indicated starting material to the target. You may use any other starting materials. The target is a mixture of diastereomers.

Starting Material = 

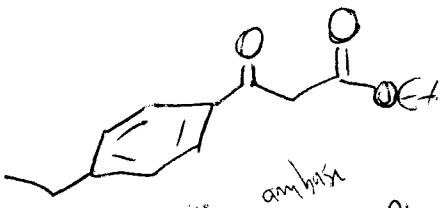
Target = 

+5

1) 1 equiv $NaOEt$, $EtOH$

EtO OEt or EtO H

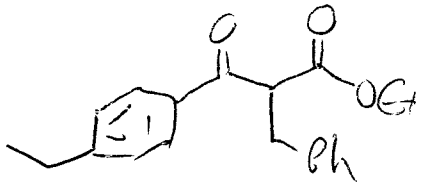
2) $H_3O^{\oplus}$



+5

amphiphile

K_2CO_3, $Ph\sim Br$



+5

amphiphile

K_2CO_3

$\sim Br$

+5

1) $LiNPN_4$

2) $H_3O^{\oplus}$

+5

[Note: Order of alkylation steps can be reversed.]