Final Exam
Chemistry 345
Professor Gellman
12 May 2015

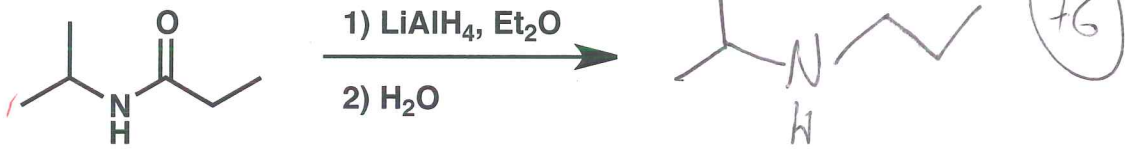
Last Name Answer

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. Models are allowed.
(ii) Print your name on each page.
(iii) Please keep your paper covered and your eyes on your own work. Misconduct will lead to failure in the course.

1. (40 points) Show the major product or products expected from each reaction.

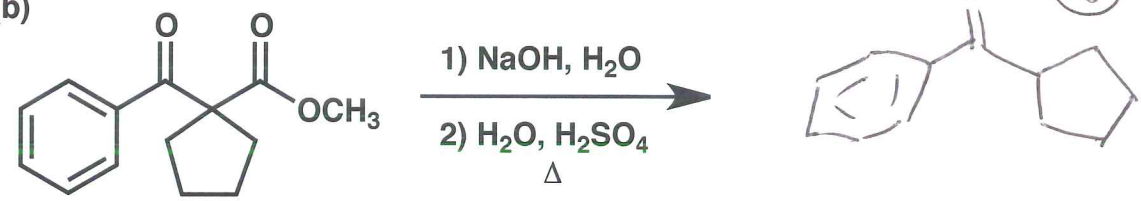
(a)



6 +6

-2 if extra proton on nitrogen

(b)

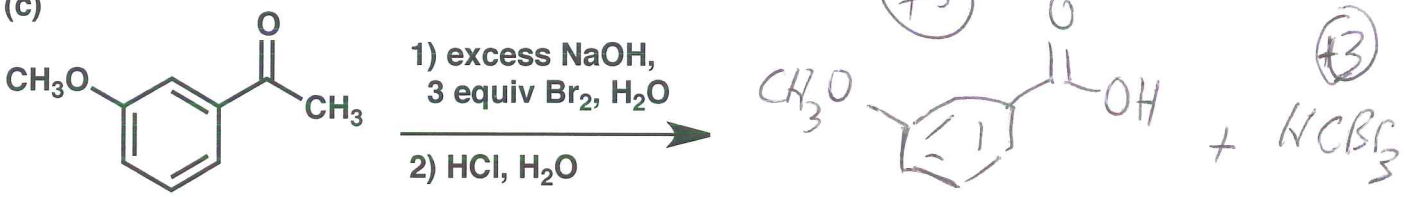


6 +6

[Not required] $+ CO_2$

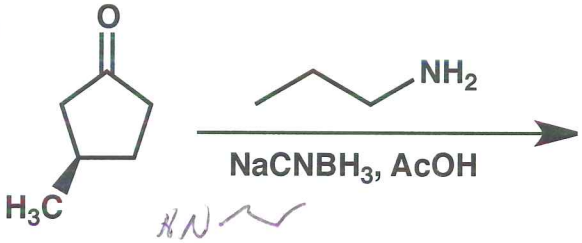
[Hint: The starting material has strong IR signals at ~1690 cm^{-1} and ~1740 cm^{-1}, but the product has only a ~1690 cm^{-1} signal (no other strong signals between 1650 and 1800 cm^{-1}).]

(c)



6 +5 +3 $+ HCBr_3$

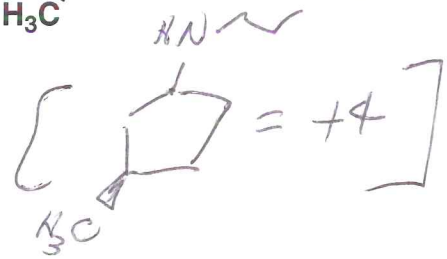
(d)



6

+

-1 if no proton



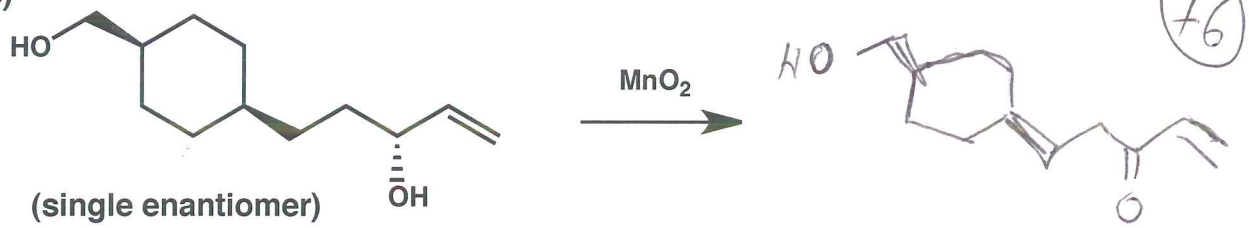
+5 for one; +8 for both

(cont. on next page)

1. (cont.)

Name Key

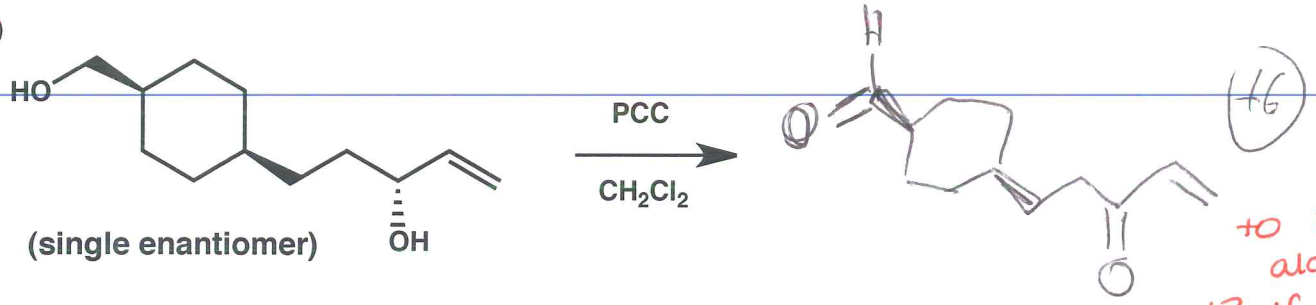
(e)



(single enantiomer)

+6

(f)



(single enantiomer)

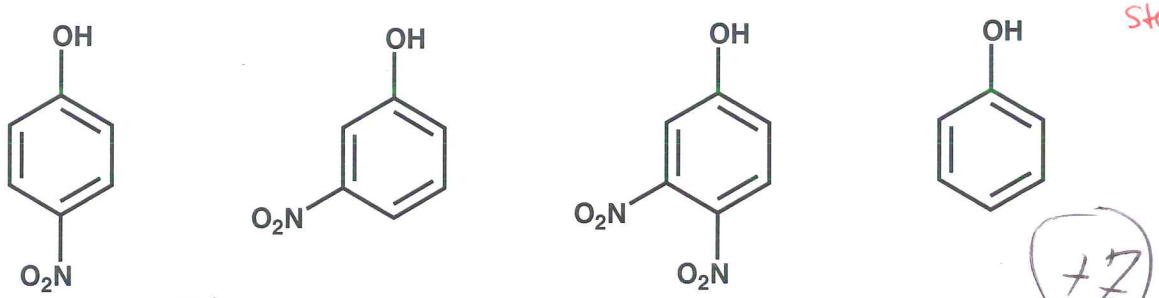
+6

+0 if any alcohol left

+3 if draw both enantiomers or if don't specify stereochem

2. (14 points) For each set of four species below, indicate the expected order of pKa values, from LOWEST (left) to HIGHEST (right).

(a)

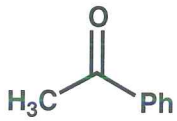


I (+2) II III IV (+2)

+7

INCREASING pKa: III < I < II < IV

(b)



V

NH3

VI

H3C—CH3

VII

HC≡CH

VIII

+7

INCREASING pKa: V < VIII < VI < VII

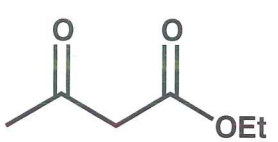
(+2) (+2)

[+2 for any "extreme" correct]

Name _____

3. (26 points) Show the reagents required to convert the starting molecule to the indicated product. If necessary, be sure to differentiate clearly between distinct steps, by using "1)," "2)," etc. over the arrow.

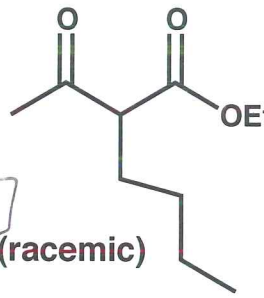
(a)



(+3) 1) NaOEt (1 equiv), EtOH

2)  [Cl-R, I-R ok]

(+3)



(racemic)

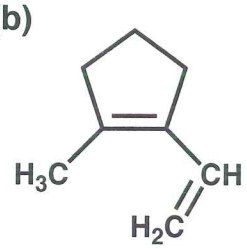
no NaOH LDA +2

-2 if one step.

-1 addition of $AlCl_3$

-1 for each additional carbon

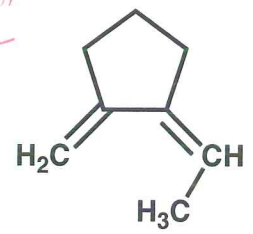
(b)



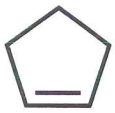
(+4) 

Δ + hν +2

-1 for addition of acid or base



(c)



(+3) 

("NBS" ok)

(+2) Δ or hν, peroxides, CCl_4

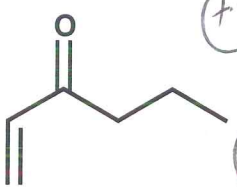
(+1)

(racemic)

NBS + Br_2 -1

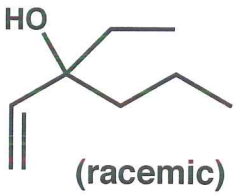
just Br_2 +0

(d)



(+4) 1)  or 

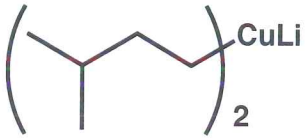
(+1) 2) H_3O^+

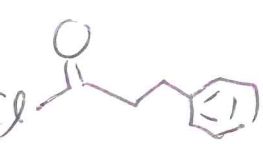


(racemic)

+3 if Grignard + acid in one step

(e)

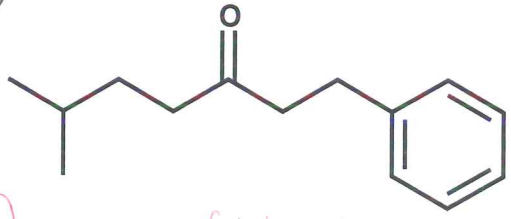


1) 

(+4) (-1)

2) H_2O (or H_3O^+)

(+1)



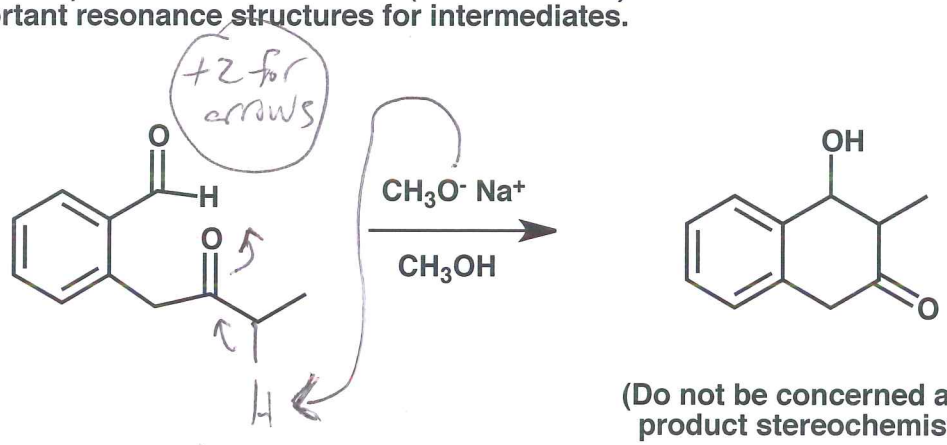
-1 addition of $AlCl_3$

-1 third step oxidation

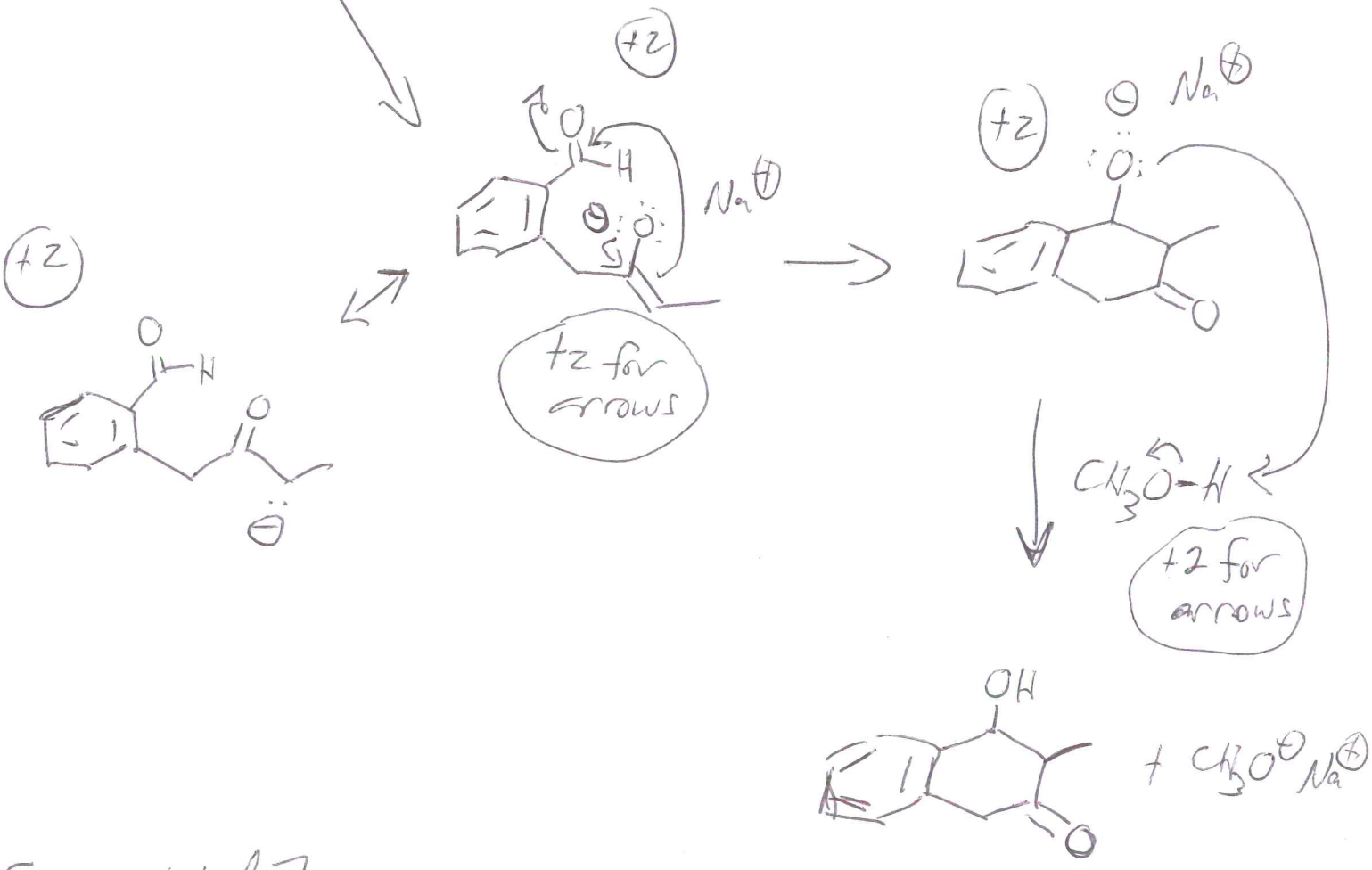
no points if ketone or aldehyde in step 1. other carboxylic acid derivative

Name _____

4. (33 points) Provide a mechanism (curved arrows) for each reaction shown below. Draw all important resonance structures for intermediates.



(Do not be concerned about product stereochemistry.)



[+12 total]

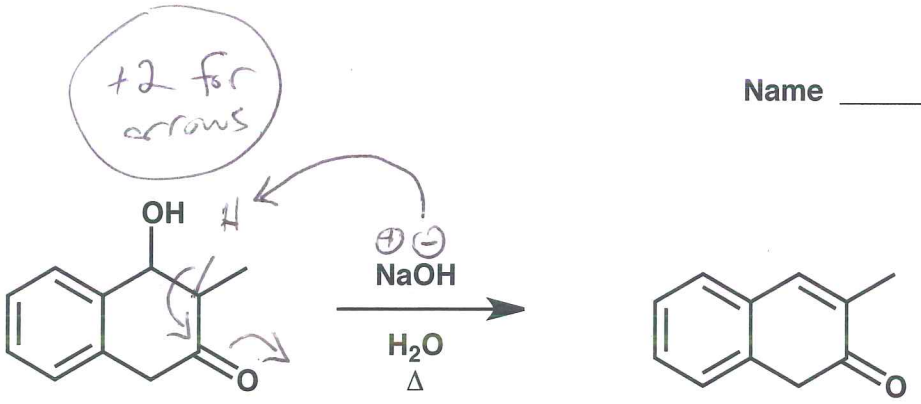
0 points for mechanism that would result in 4-membered ring

(cont. on next page)

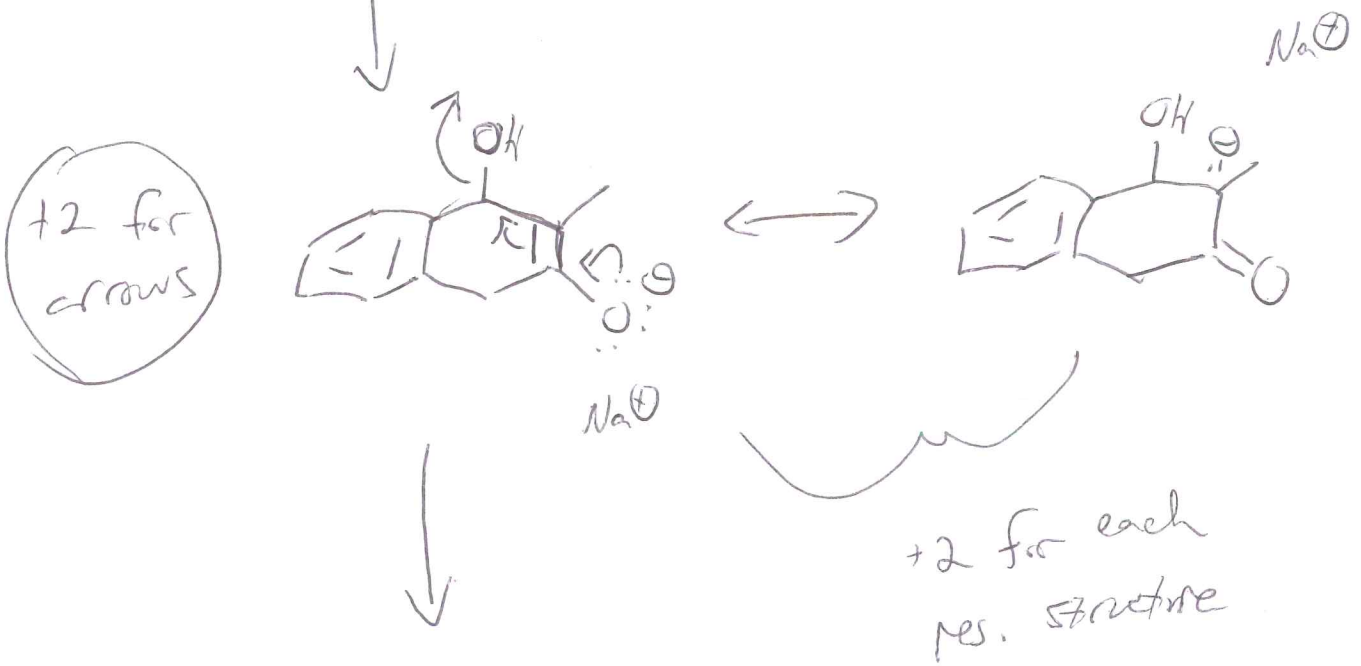
Name _____

4. (cont.)

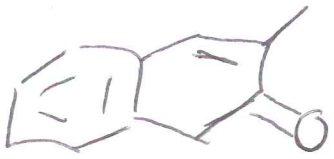
(b)



(Do not be concerned about stereochemistry.)



+2 for each res. structure



+

$Na^{\oplus}\ ^{\ominus}OH$

[+8 total]

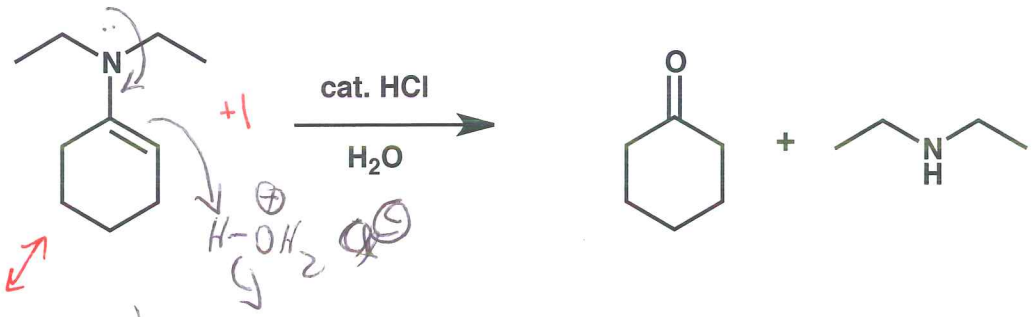
0 points for E Z

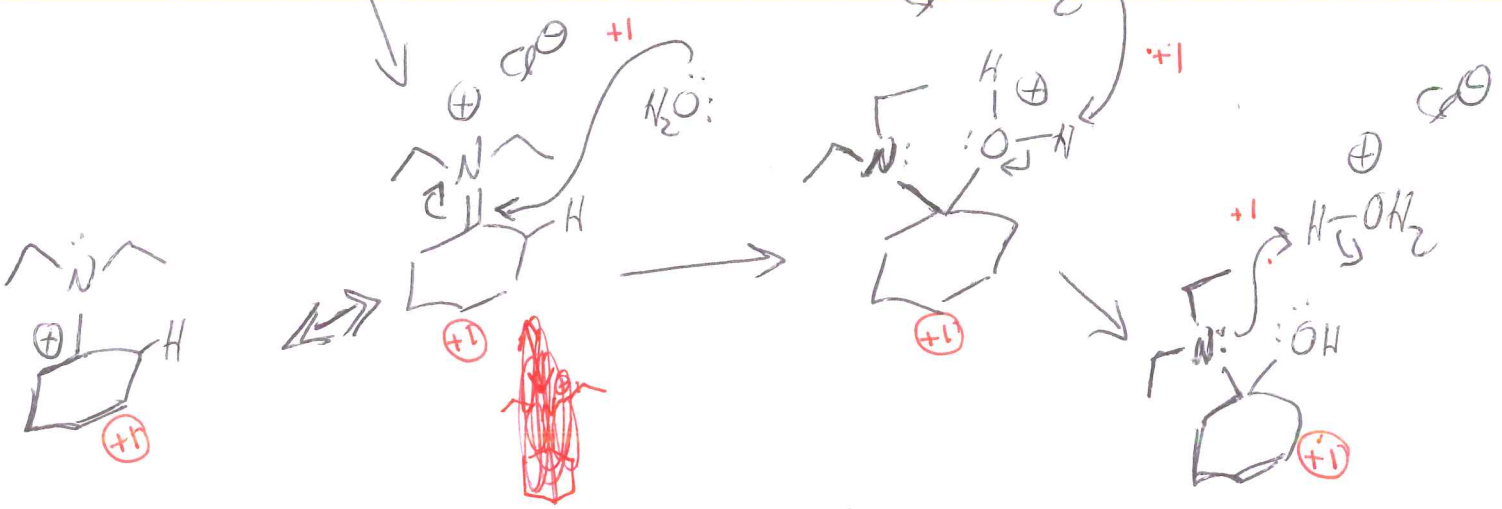
(cont. on next page)

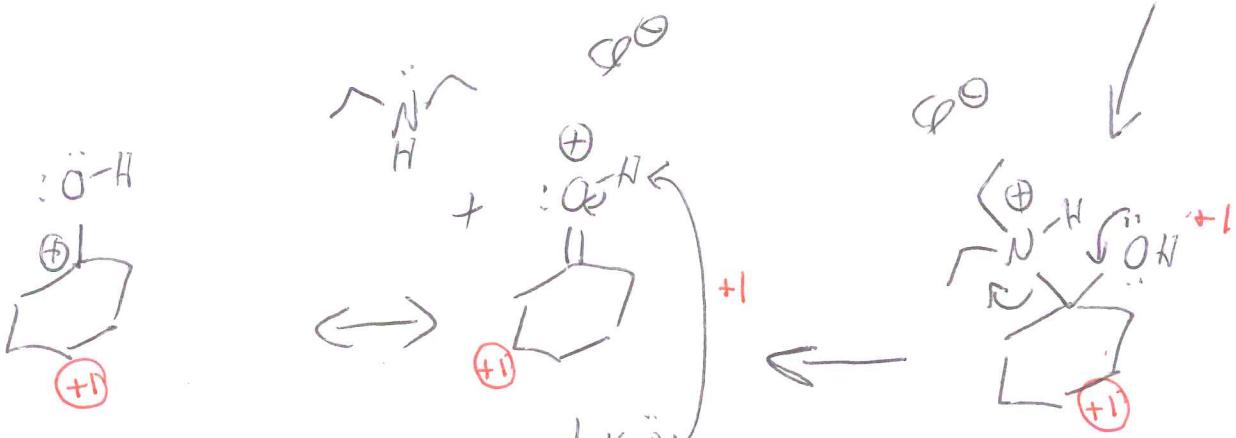
Name _____

4. (cont.)

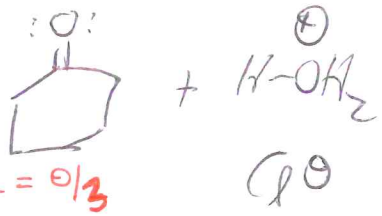
(c)







[ok if the amine is the base here.]



- If protonate/deprotonate @ same time = ⊖/3
- Intramolecular proton transfer OK (full credit) ⇒ if do proton transfer + amine leaving all in one step = no points

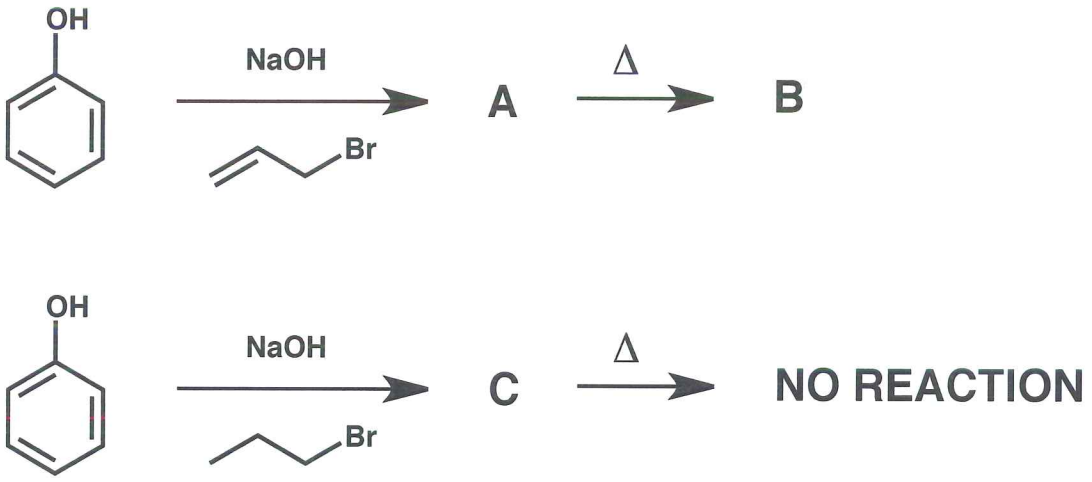
+1 for each intermediate structure (incl. res. structures): +7 total

+1 for each set of arrows: +6 total

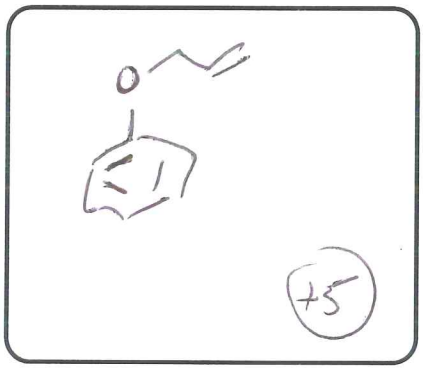
Name _____

5. (cont.)

(b)



A =



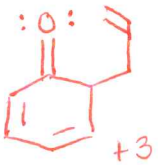
^{1}H NMR spectrum includes:

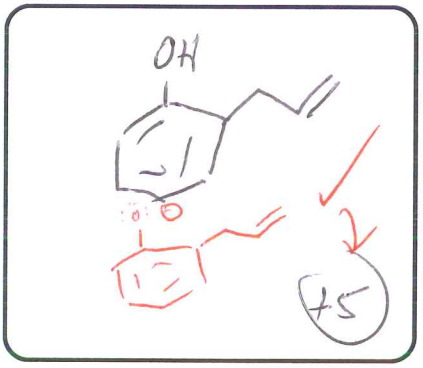
3 signals 6.8-7.2 ppm (2H, 2H, 1H)*

3 signals 5.0-6.0 ppm (1H each)

1 signal ~4 ppm (2H)

B =





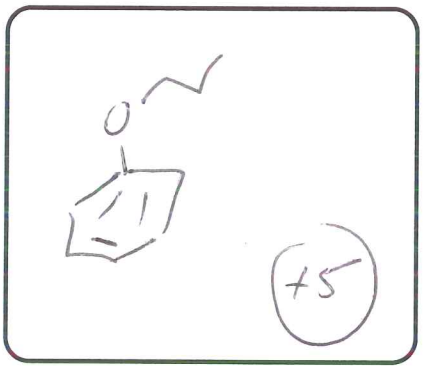
^{1}H NMR spectrum includes:

4 signals 6.8-7.2 ppm (1H each)*

3 signals 5.0-6.0 ppm (1H each)

1 signal ~3.5 ppm (2H)

C =



^{1}H NMR spectrum includes:

3 signals 6.8-7.2 ppm (2H, 2H, 1H)*

1 signal ~3.5 ppm (2H)

1 signal ~1.6 ppm (2H)

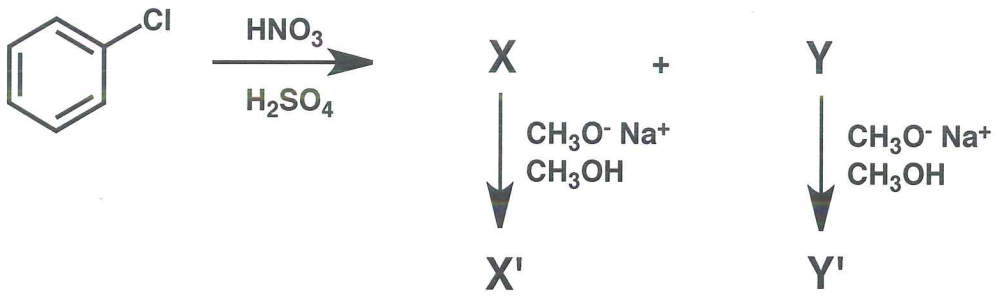
1 signal ~1.0 ppm (3H)

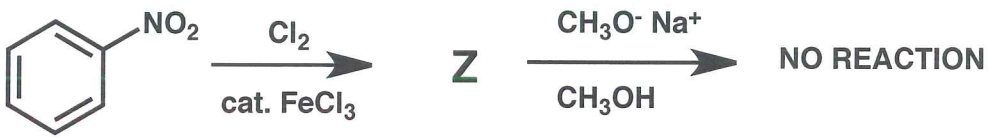
* Note: "1H" means that the integration corresponds to 1 proton, etc.

Name _____

5. (36 points) For each reaction or set of related reactions shown below, draw the structures of the indicated products in the boxes. Your structures must be consistent with the spectroscopic data given for these compounds.

(a)





In the boxes below, provide structures for molecules X, Y, Z, X' and Y' that are consistent with the following spectroscopic data.

-- The ^{13}C NMR spectrum of X has FOUR resonances, all with $\delta > 100$.

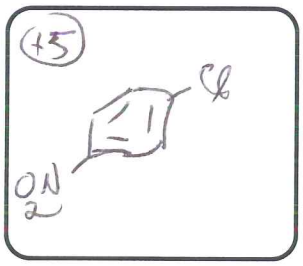
-- The ^{13}C NMR spectrum of X' has FIVE resonances, four with $\delta > 100$ and one with $\delta < 80$.

-- The ^{13}C NMR spectrum of Y has SIX resonances, all with $\delta > 100$.

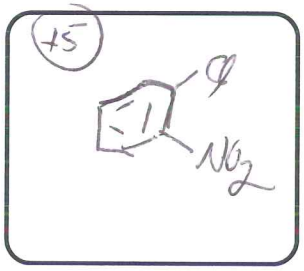
-- The ^{13}C NMR spectrum of Y' has SEVEN resonances, six with $\delta > 100$ and one with $\delta < 80$.

-- The ^{13}C NMR spectrum of Z has SIX resonances, all with $\delta > 100$.

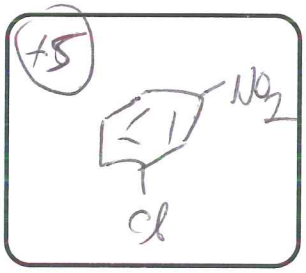
X =



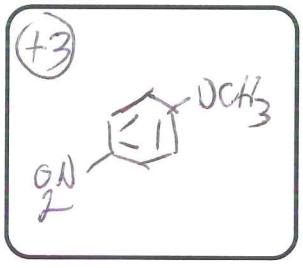
Y =



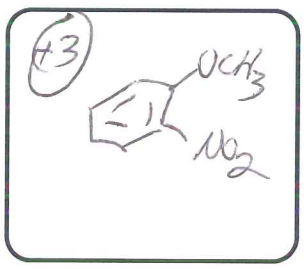
Z =



X' =



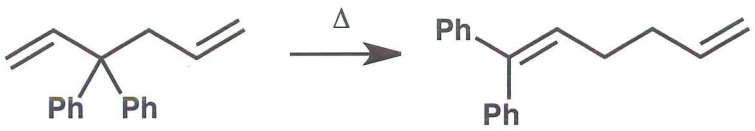
Y' =



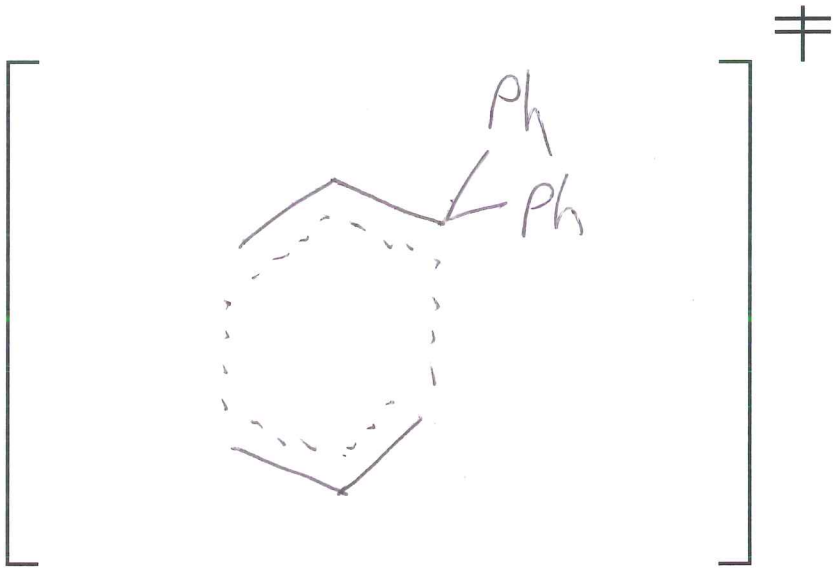
-- cont. on next page --

Name _____

6. (10 points) Shown below is an example of a [3,3]-sigmatropic rearrangement.



Draw the transition state for this reaction below, using dotted lines to indicate bonds that are forming or breaking.



Name _____

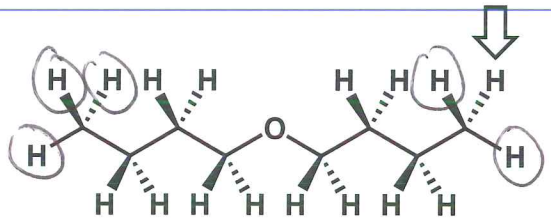
7. (9 points)

For each molecular drawing below, with reference to the H indicated by the arrow, label other H's as directed below.

Put a CIRCLE around any homotopic H's.

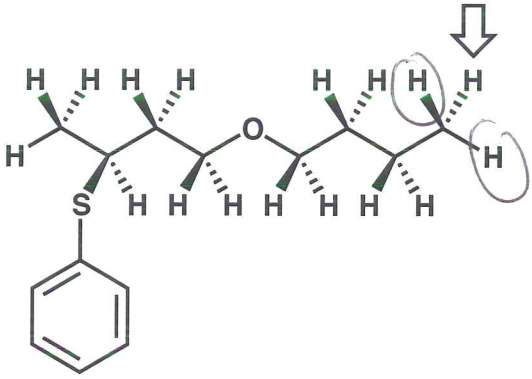
Put a TRIANGLE around any enantiotopic H's.

Put a SQUARE around any diastereotopic H's.

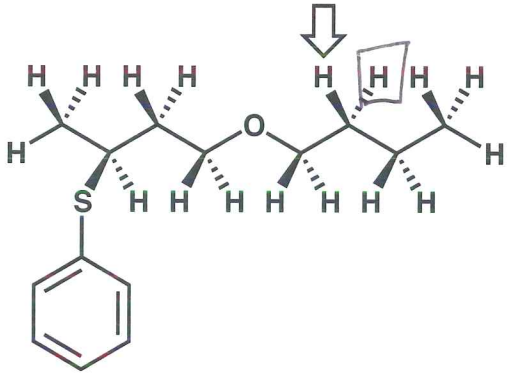


+1 each [+5]

[-1 for extraneous designations]



+1 each [+2]



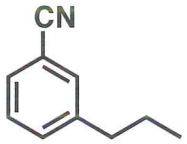
+2

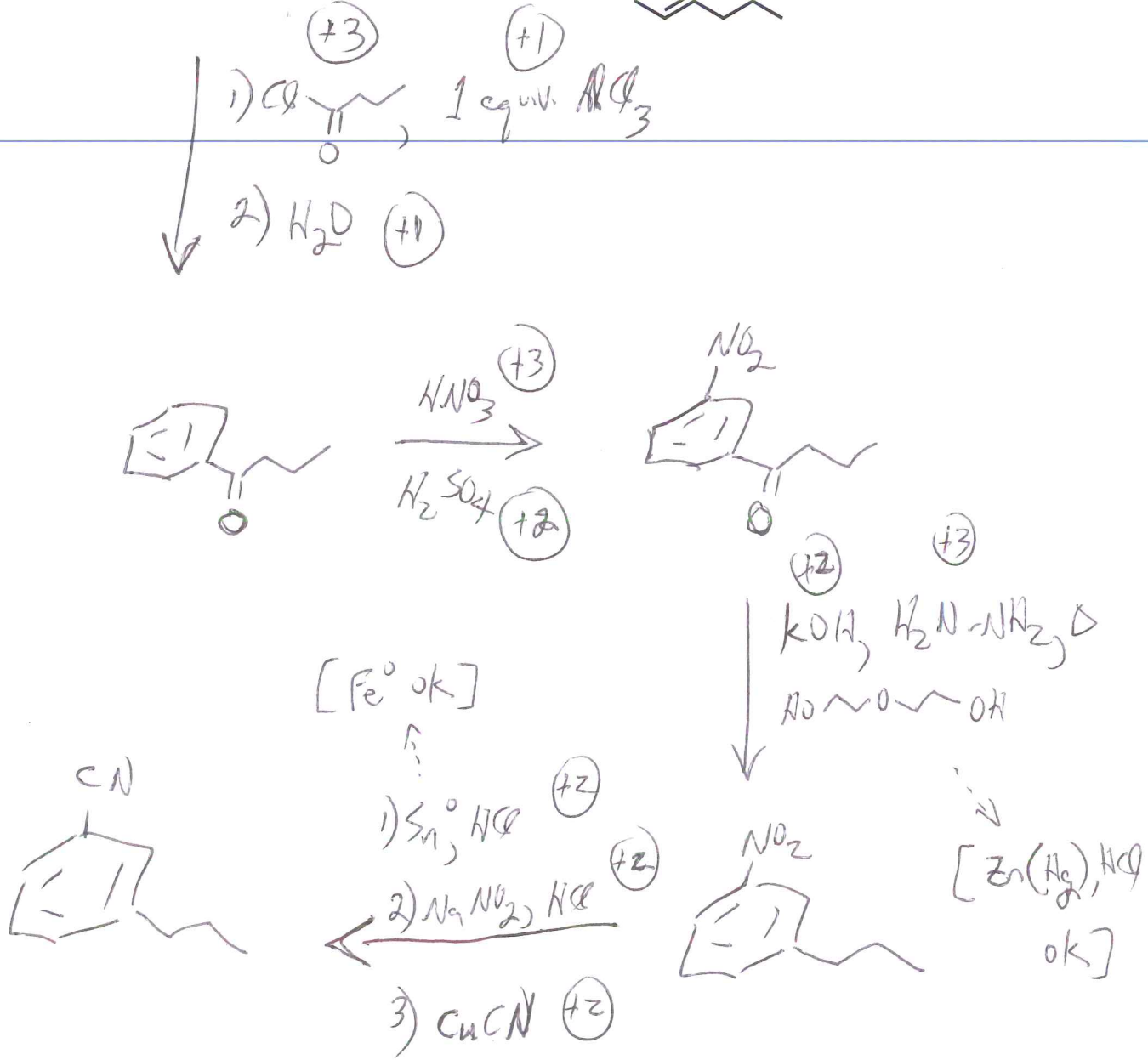
Name _____

8. (32 points)

(a) Propose an efficient synthetic route from the indicated starting material to the target. You may use any other starting materials containing 3 or fewer carbons, and any reagents.

Starting material = 

Target = 



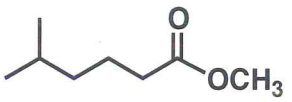
[+ 21 total]

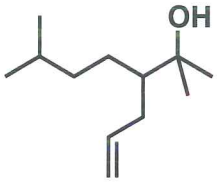
-- cont. on next page --

Name _____

8. (cont.)

(b) Propose an efficient synthetic route from the indicated starting material to the target. You may use any other starting materials containing 3 or fewer carbons, and any reagents.

Starting material = 

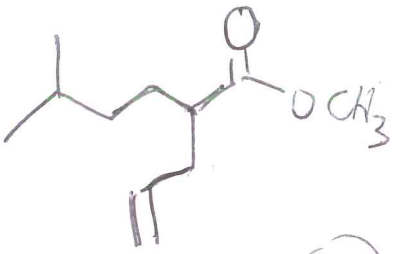
Target = 

(racemic)

(+3) 1) $Li^{\oplus}\ ^{\ominus}N(i\text{-}Pr)_2$ ["LDA" ok]

NaOEt + ∅ but still get points for correct Electrophile

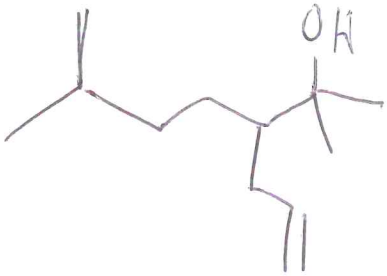
(+3) 2) Br 



If they make acyl chloride then MeLi get +3 *essentially 2 for missing two steps

(+2) 1) 2 equiv. CH_3Li [CH_3MgX ok] (+3)

2) $H_3O^{\oplus}$



[+11 total]