Hour Exam #3
Chemistry 345
Professor Gellman
27 April 2016

Last Name Answer

First Name Key

General Instructions:

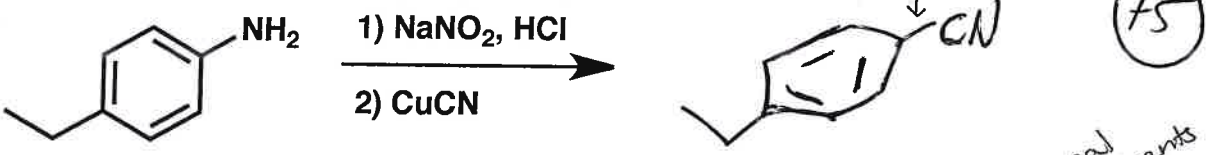
(i) Use scratch paper at back of exam to work out answers; final answers must be recorded at the proper place on the exam itself for credit. Models are allowed.

(ii) Print your name on each page.

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

1. (16 points) Show the ORGANIC product(s) expected from the reactions indicated below.

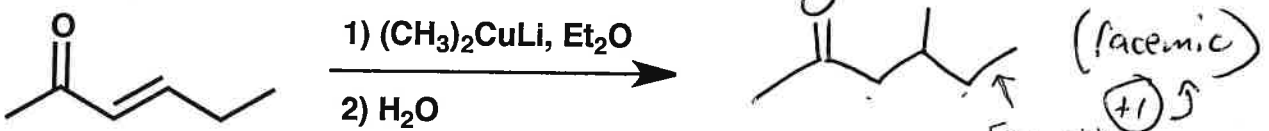
(a)



If shown as wedge or dash, +2

+5

(b)



any additional substituents (-1)

+5

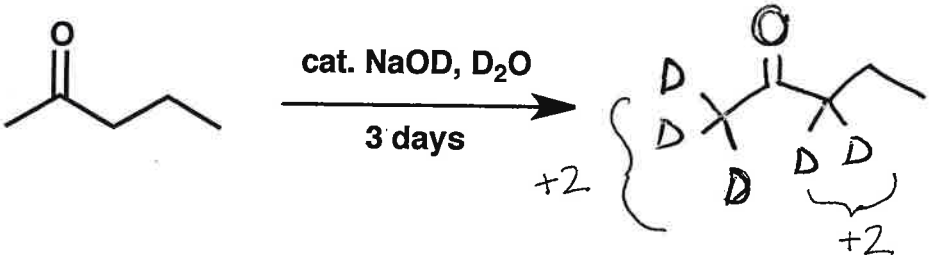
(racemic)

+1

Forgetting this carbon (-1)

any addition at incorrect carbon, no points for whole problem 1.b

(c)



+5

If correctly labelled only one carbon, +2.

If any carbons labelled incorrectly, 0.

[Hint: The starting material and product for part (c) have nearly identical ^{13}C NMR spectra. The product ^{1}H NMR spectrum has only two signals, a multiplet at δ0.93 (3H) and another at δ1.60 (2H).]

-2 if out of sequence (or sequence not indicated) | -2 for incorrect # Cs

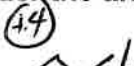
-3 if added a ~~bad~~ bad reagent, and everything else is right

Name _____

2. (30 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.

5

(a)

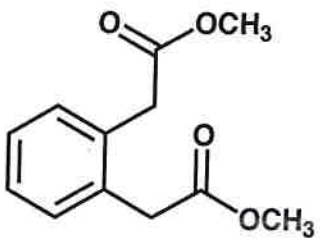
1) (+4)  [Not required]

2) HCl, H_2O [$H_3O^\oplus$ or H_2O ok] (+1)

(+0 for Grignard)

5

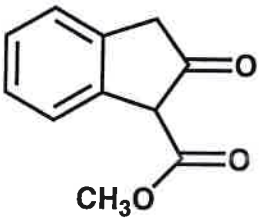
(b)



(+1) (+3) (+1 for NaOEt/EtOH)

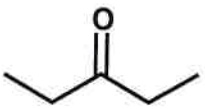
1) 1 equiv. $NaOCH_3$, CH_3OH

2) HCl, H_2O [$H_3O^\oplus$ ok] (+1)

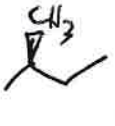


7

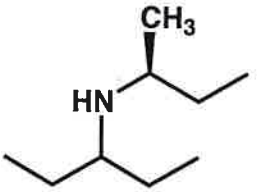
(c)



+1 for no stereochem

(+3)  , $NaBH_3CN$ (+3)

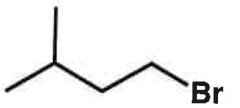
AcOH (+1)



(single enantiomer)

6

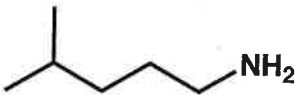
(d)



(+1 for HCN) (+3)

1) NaCN, DMSO [Not required]

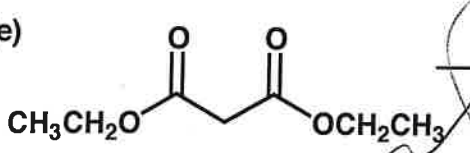
2) $LiAlH_4$ (+3) or H_2, Raney Ni (+3) (+1)



[Not required] → 3) $H_3O^\oplus$ 4) NaOH

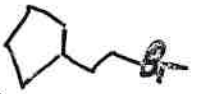
7

(e)

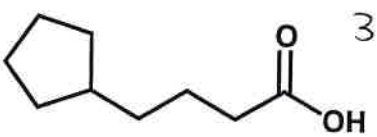


(+1) (+2)

1) 1 equiv. NaOEt, HOEt

2)  (+2)

No NaOH before step 3!



[ok if in same step] H_3O^+

3) NaOH, H_2O (+1)

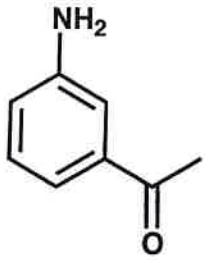
4) HCl, H_2O, Δ (+1)

"$H_3O^\oplus$" ok ~~need~~

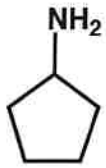
ok if just "$H_3O^\oplus$, Δ" -+2

Name _____

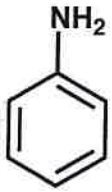
3. (6 points) Indicate the order of basicity of compounds W-Z, from MOST BASIC on the LEFT to LEAST BASIC on the RIGHT.



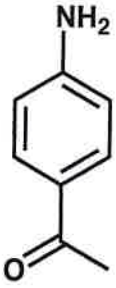
W



X

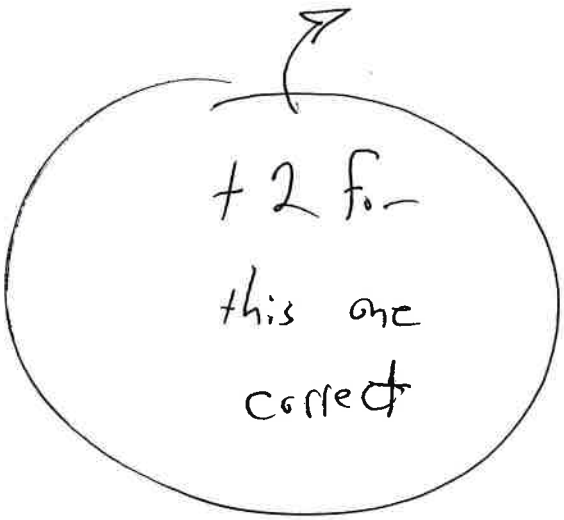


Y



Z

Basicity: X > Y > W > Z

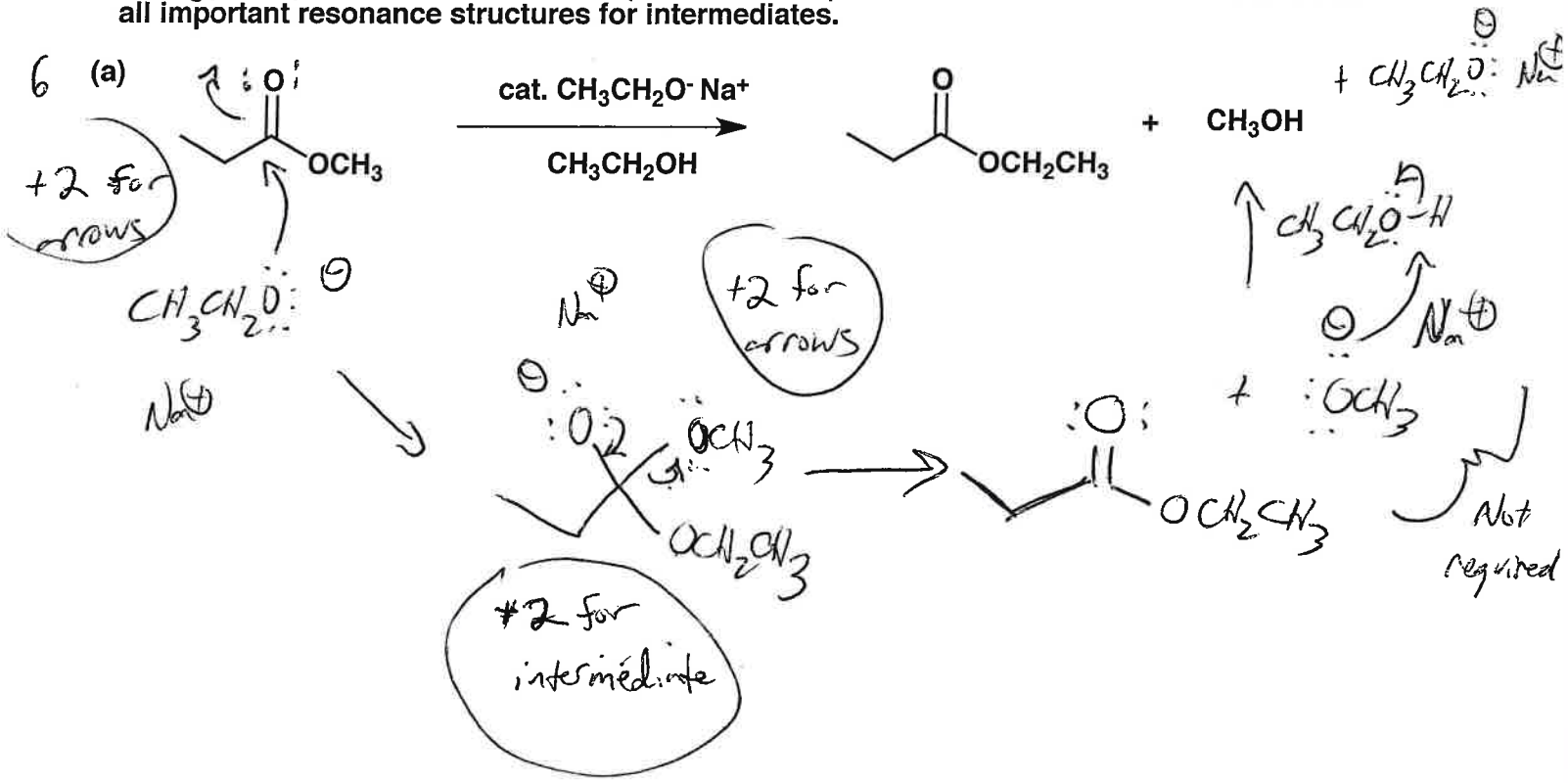


+2 for this one correct

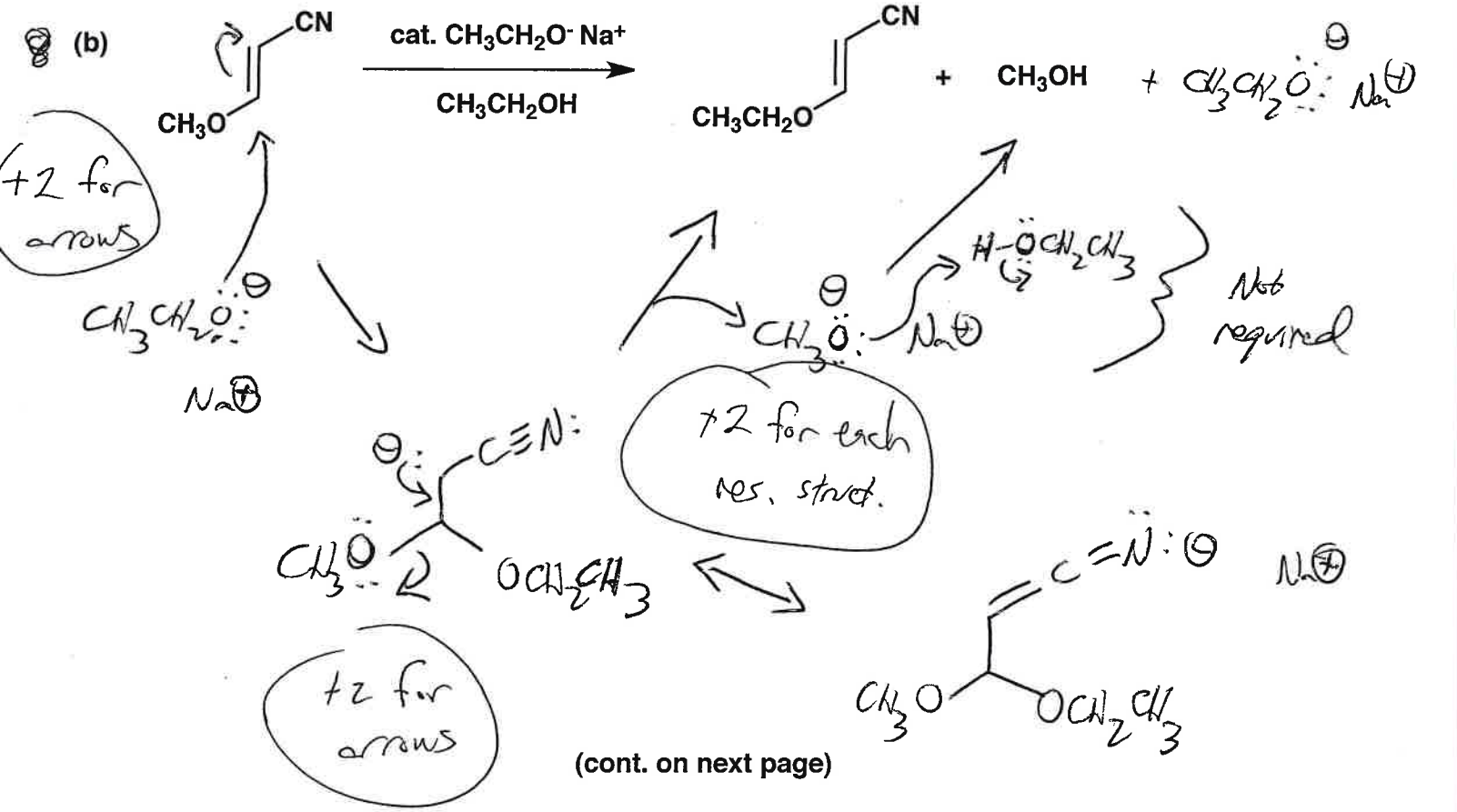
Name _____

4. (25 points) Provide a mechanism (curved arrows) for each reaction shown below. Draw all important resonance structures for intermediates.

6 (a)



(b)



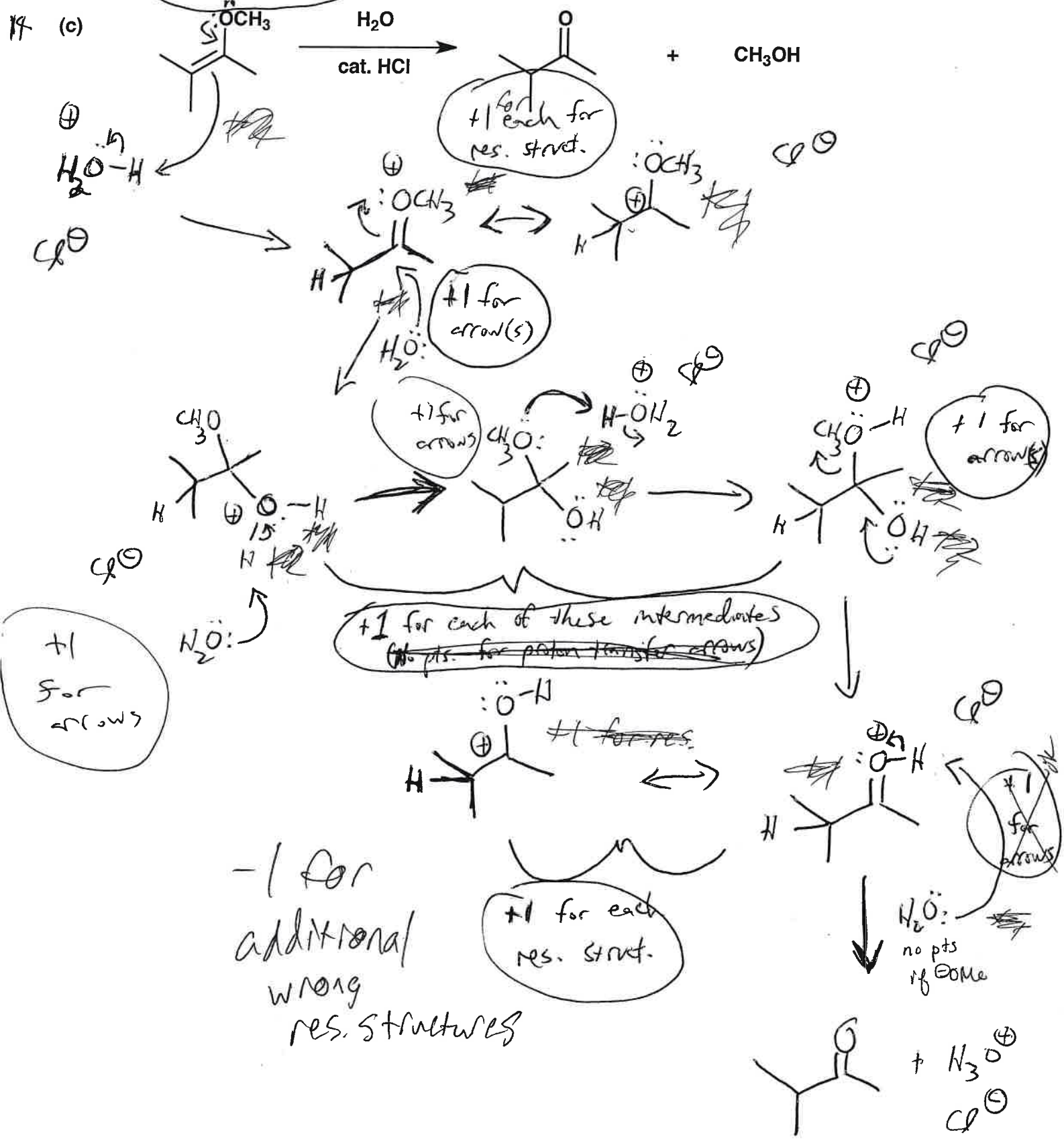
(cont. on next page)

Name _____

4. (cont.)

+2 for arrows (2 or 3)

14 (c)

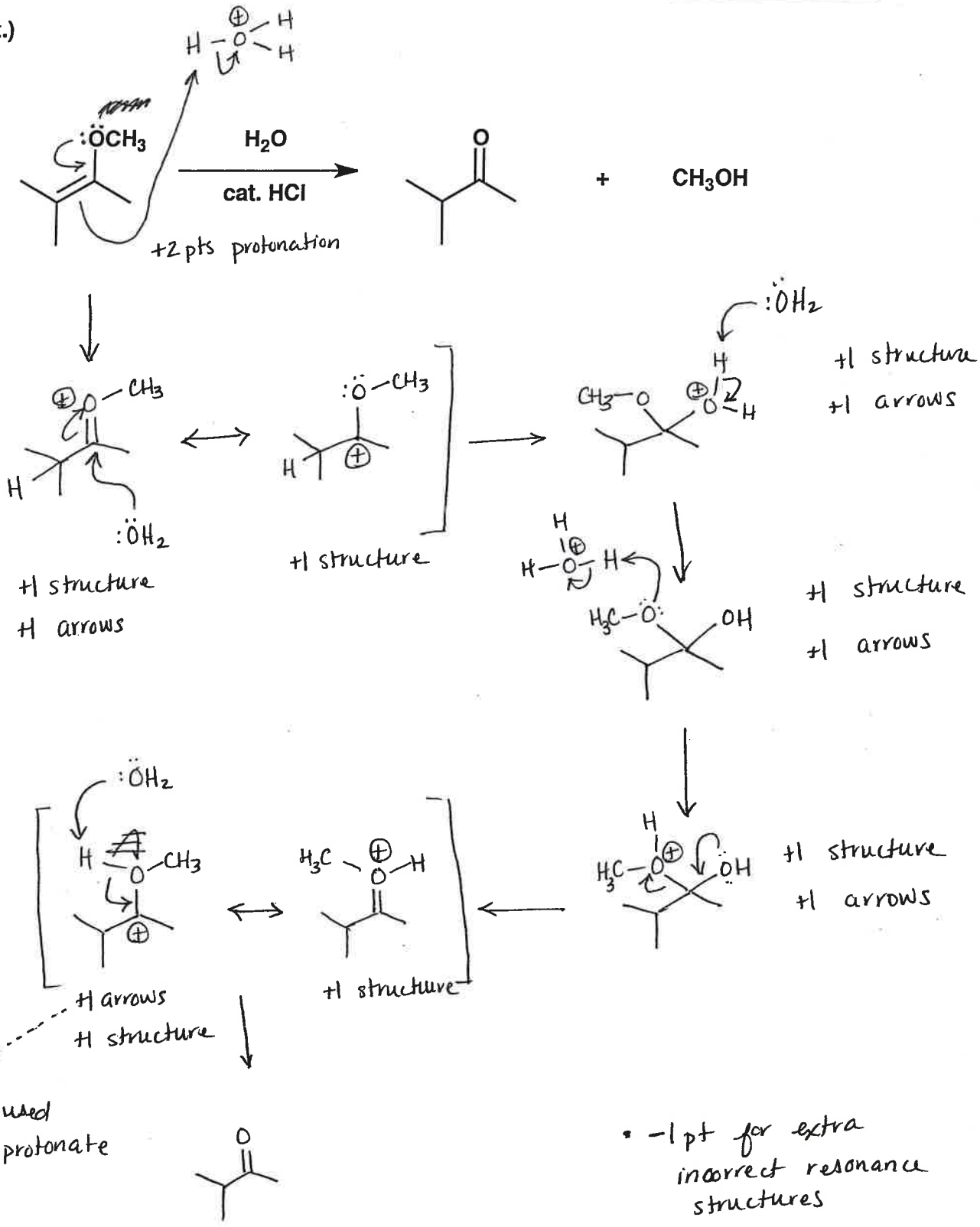


-1 for additional wrong res. structures

14

4. (cont.)

(c)

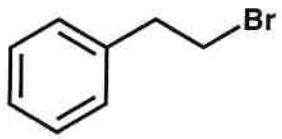

H2O
cat. HCl
CH3OH
+2 pts protonation
+1 structure
+1 arrows
+1 structure
+1 structure
+1 arrows
+1 structure
+1 arrows
+1 structure
+1 arrows
+1 structure
+1 arrows
+0 if ⊖OMe used to deprotonate
• −1 pt for extra incorrect resonance structures
• −1 pt for missing formal charges

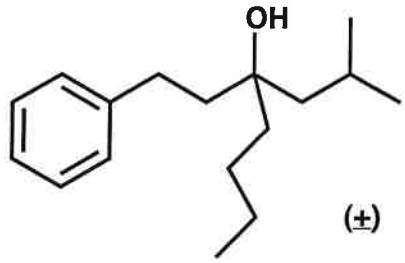
max for using a 5 carbon unit is 15/20

Name _____

5. (20 points)

Propose an efficient synthetic route from the indicated starting material and any reagents or other organic molecules with FOUR or fewer carbons.

Starting material = 

Target = 

(±)

-1 overall if carbon count is off consistently

(+5)

1) Mg^0, Et_2O (+2) if only make grignard

2) CO_2

3) H_2O, HCl

(+5)

$SOCl_2$ or PCl_5 or $POCl_3$

(+5)

1) (R_2CuLi)

2) H_2O

or +2 for just that

1) ^-CN

2) Nitrile hydrolysis

+5

OK to reverse cuprate + organolithium or Grignard reagents

or

Pd/C poisoned H_2

1) RM

2) $H_3O^\oplus$

[ox] (-3 if mess up ox)

1) R_2M 2) $H_3O^\oplus$

product

(+5)

1) Li [Grignard oks]

2) H_2O, HCl