Final Exam
Chemistry 345
Professor Gellman
11 May 2014

Last Name Answer

First Name key

General Instructions:

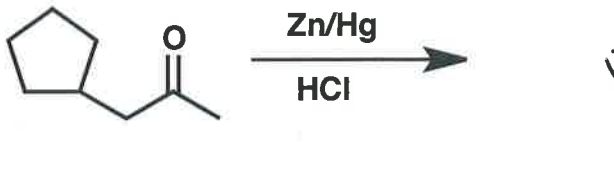
(i) Use scratch paper at back of exam to work out answers; final answers must be recorded at the proper place on the exam itself for credit. Models are allowed.

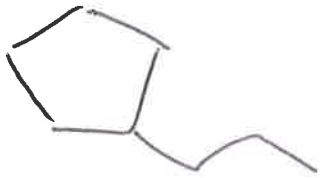
(ii) Print your name on each page.

(iii) Please keep your paper covered and your eyes on your own work. Misconduct will lead to failure in the course.

1. (32 points) Show the major product or products expected from each reaction.

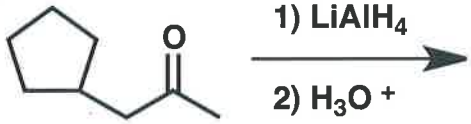
(a)





+5

(b)

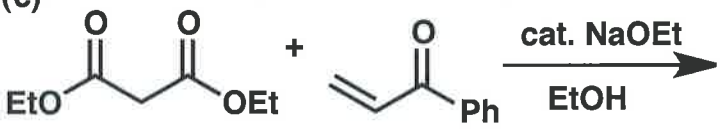


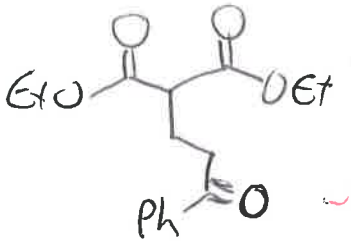
+5

(racemic) ← [Not required]

+2 missing carbon

(c)

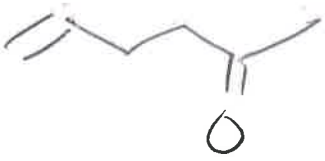




+5

−1 for extra structure or missing Ph

(d)



+5

−1 for extra structure

missing double bond +0 or double bond in wrong place

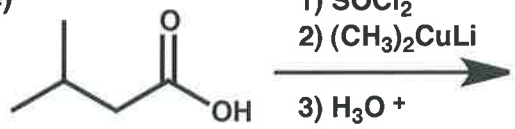
[Hint: The product has a strong IR signal at 1720 cm^{-1}, but the starting material does not.]

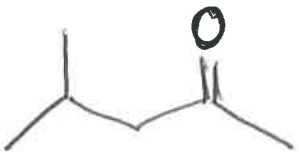
(continued on next page)

1. (cont.)

Name _____

(e)

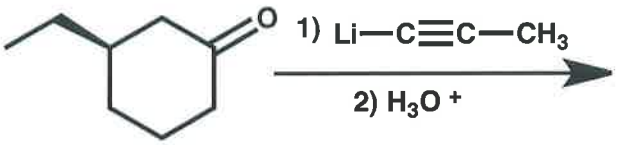


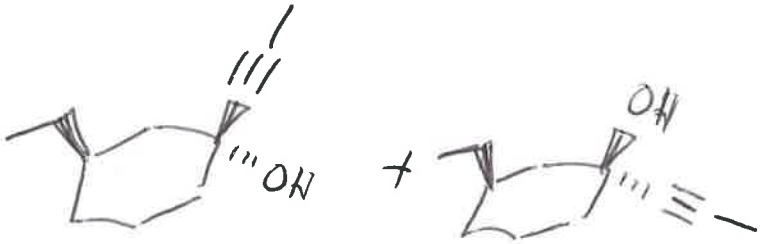


+5

−2 missing carbon (additional) or wrong branching

(f)





(Single enantiomer)

+2 if shift over groups w/ correct

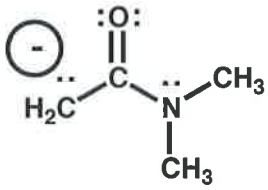
−2 missing stereo carbon

+0 shifted and no stereochem

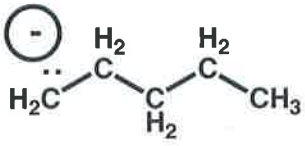
+4 for one; +7 for both

[+3 for structure w/o proper stereochem]

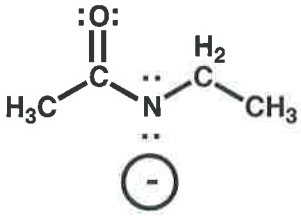
2. (8 points) Rank the four anions below (A, B, C and D) in terms of basicity, with the STRONGEST base on the RIGHT.



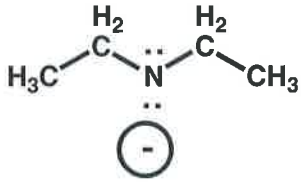
A



B



C



D

INCREASING basicity to the RIGHT:

C < A < D < B

+2 or

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

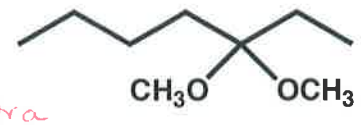
+2

+8 for all 4 correct

Name _____

3. (30 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)



HOCH3, H2SO4 ⇒ +4

(+2) Cat. NCl

(+2) N2O

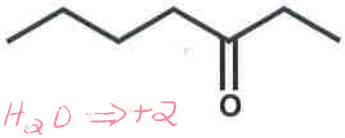
any extra oxidizing agent −1

1) H3O+ ⇒ +4

Any strong acid ok, or "H⊕"; "cat." not required

NaOH, H2O ⇒ +2

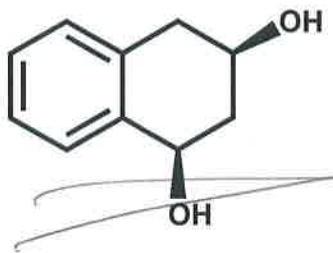
1) NaOH
2) H3O+ } +2



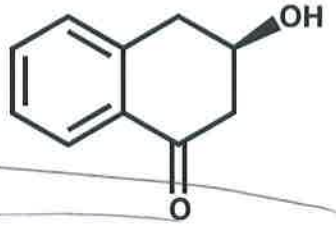
+ 2 CH3OH

MnO4 ⇒ +1 PCC ⇒ +2 Mn2O ⇒ +3

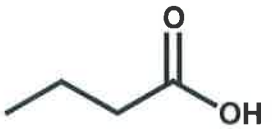
(b)



MnO2 (+4)



(c)



(+9) 1) LiAlH4, Et2O

2) H2O or H3O⊕

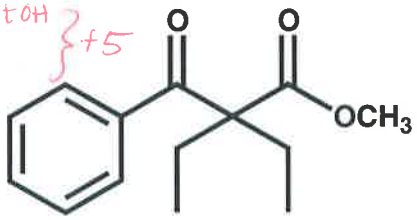
1) Br2, NaOH
2) H3O+ → +0

(+1) OR: NaOCH3, CH3OH (+8)

all one step ⇒ +7

EtOH

(d)



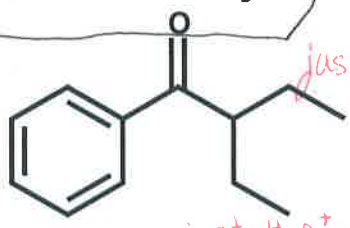
1) NaOEt, EtOH
2) NaOH
3) H3O+, Δ } +5

H3O+, Δ ⇒ +8

(+2) 1) NaOH, H2O (+2)

2) H3O⊕, Δ

(+2) (+2)



H3O+, H2O ⇒ +2

just NaOCH3 ⇒ +1

just H3O+, H2O ⇒ +2

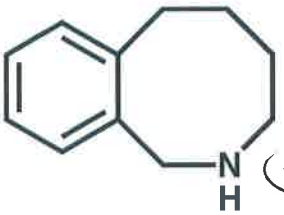
(+3) 1) Excess CH3I

2) Ag2O, H2O

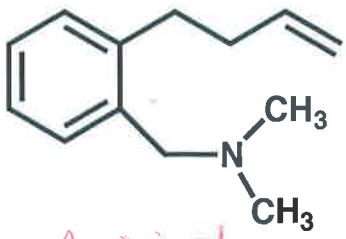
3) Δ (+3)

no excess −1 CH3Br +2

(e)



(+3)

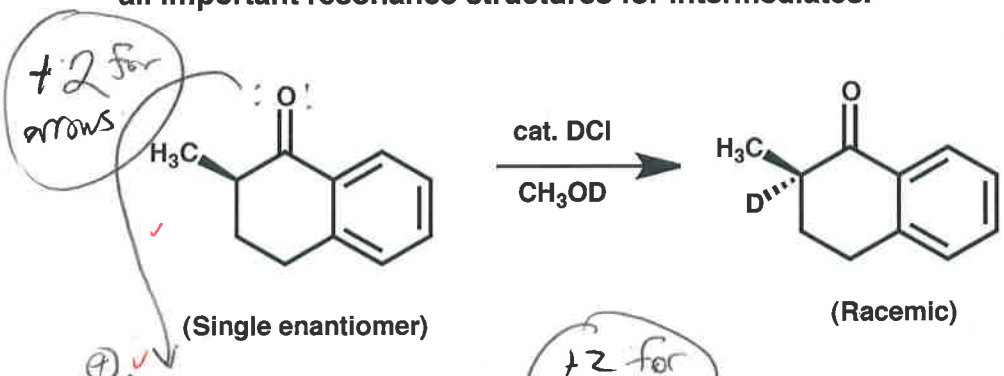


combine Ag2O, Δ −1

1) Ag2O
2) CH3-I } +2

Name _____

4. (30 points) Provide a mechanism (curved arrows) for each reaction shown below. Draw all important resonance structures for intermediates.



[Ok if res. structures involving ring are shown, but not required.]

[Note: ok if DCl is acid]

+2 for arrows

+1 for each res. structure

+2 for arrows

+2 for arrows

+1 for each structure (14 altogether)

(racemic)

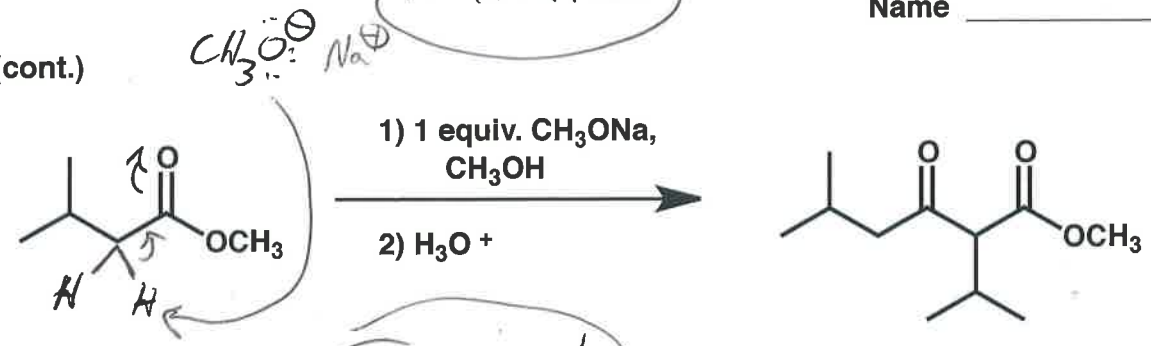
(cont. on next page)

+14 total

Name _____

4. (cont.)

(b)



+2 for arrows

+1 for each res. structure

+2 for arrows

(10/16 for up to here)

+2 for arrows

+2 for intermediate

+1 for intermed.

+2/6 for

+2 for arrows

+1 for each res. structure

Add

+1 for arrows

0/6 for all acid mechanism

-1 for missing formal charges

-1 for extra, incorrect resonance structures

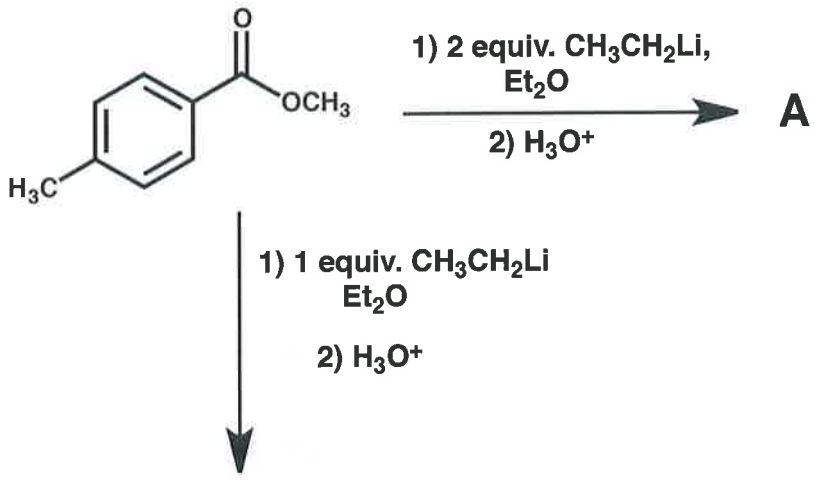
-1 for incorrect use of resonance vs. reaction arrows

+16 total

Name _____

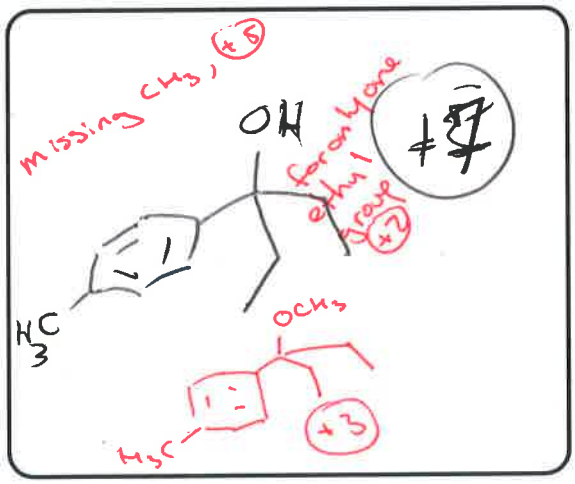
5. (28 points) For each reaction or set of related reactions shown below, draw the structures of the indicated products in the boxes. Your structures must be consistent with the spectroscopic data given for these compounds.

(a)



A + B + recovered starting material

A =



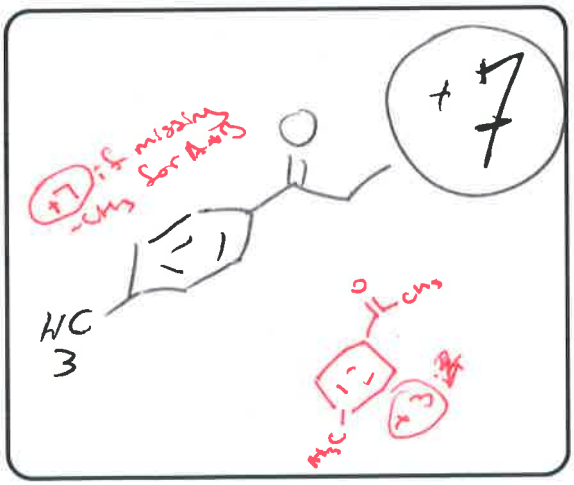
Strong IR signal at 3350 cm^{-1}

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

^1H NMR shows one resonance that disappears after shaking with D_2O.

^1H NMR resonances that remain after D_2O shake include two doublets that together integrate to 4 H in the range 7-8 ppm, and a triplet and a quartet below 2.5 ppm that together integrate to 10 H.

B =



No IR signal > 3100 cm^{-1}

Strong IR signal at 1685 cm^{-1}

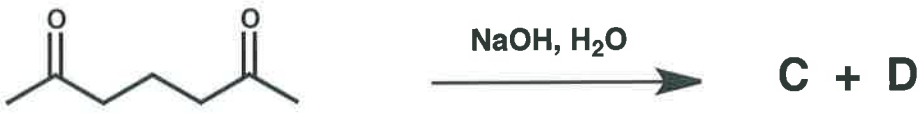
^1H NMR resonances include include two doublets that together integrate to 4 H in the range 7-8 ppm, and a triplet and a quartet below 2.5 ppm that together integrate to 5 H. None disappears on shaking with D_2O.

-- cont. on next page --

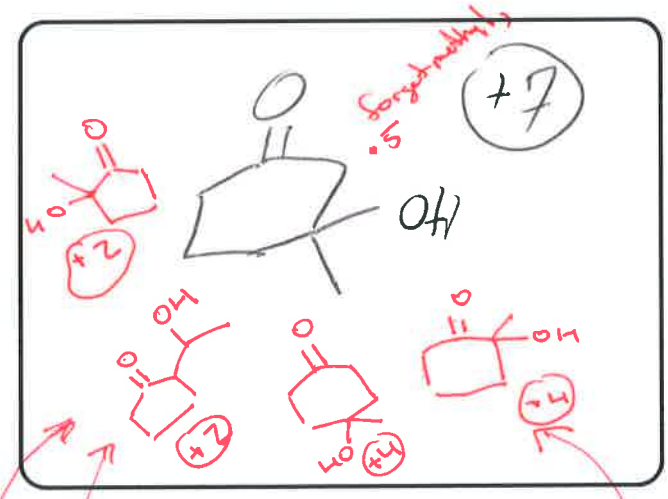
Name _____

5. (cont.)

(b)



C =



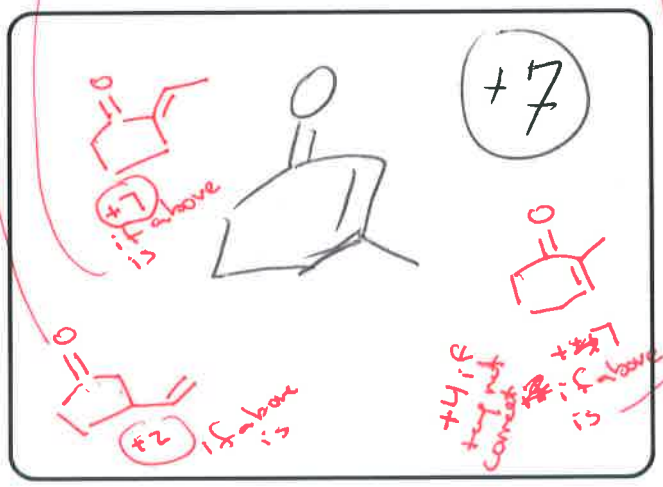
Strong IR signal at 1710 cm^{-1}

Strong IR signal at 3350 cm^{-1}

^1H NMR shows one resonance that disappears after shaking with D_2O.

^1H NMR resonances that remain after D_2O shake are all < 3 ppm.

D =



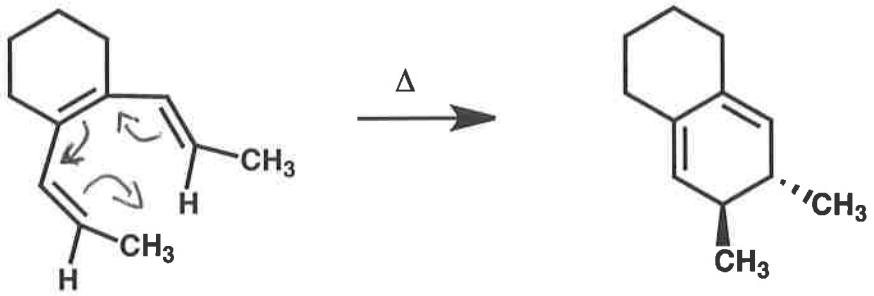
Strong IR signal at 1680 cm^{-1}

No IR signal > 3100 cm^{-1}

^1H NMR resonances include one in the range 4.5-6.0 ppm; the rest are below 3 ppm. None disappears on shaking with D_2O.

6. (15 points) Name _____

(a) Provide a mechanism (curved arrows) for the reaction below.

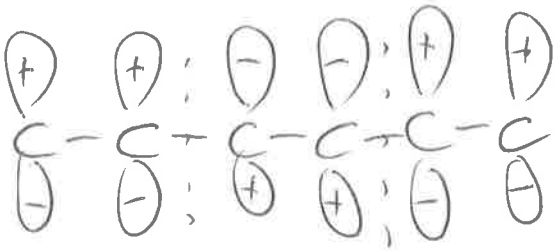


(racemic)

+3

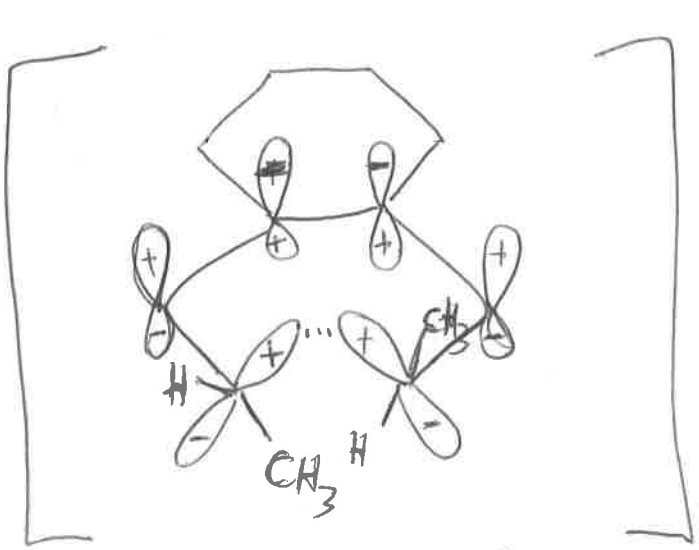
(b) Provide a drawing that shows the symmetry of the π molecular orbital that controls this reactivity. This drawing should focus only on the π system, and not include any substituents.

+5



[Dotted lines (nodes) not required]

(c) Provide a drawing that shows the the π molecular orbital from part (b) superimposed on the molecule at the transition state for this reaction. This drawing should provide a rationale for the stereochemistry of the product.



correct "bonding" relationship for new σ-bond = +4

Methyl groups headed toward "trans" = +3

Name _____

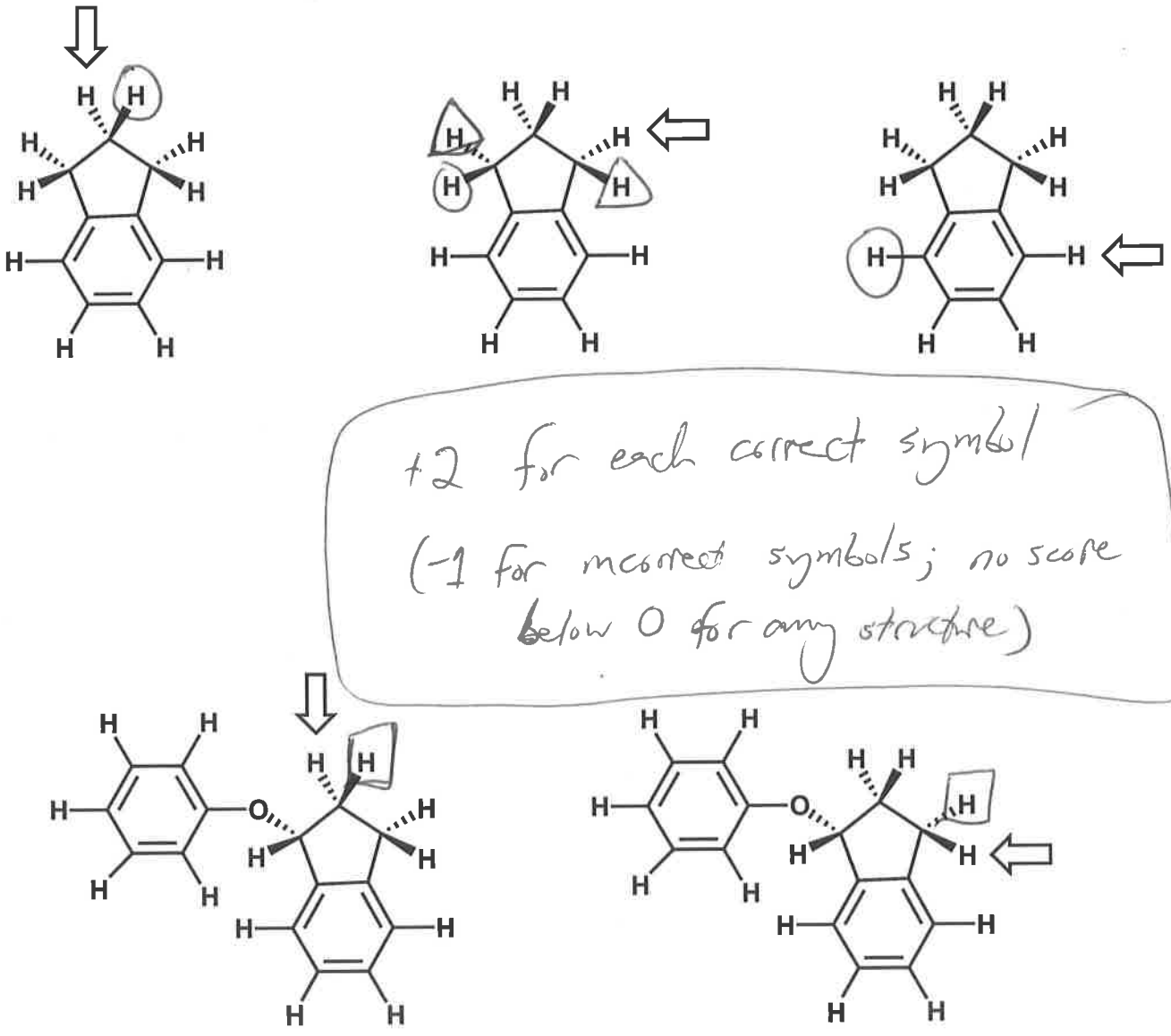
7. (14 points)

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

...Put a CIRCLE around any homotopic H's.

...Put a TRIANGLE around any enantiotopic H's.

...Put a SQUARE around any diastereotopic H's.

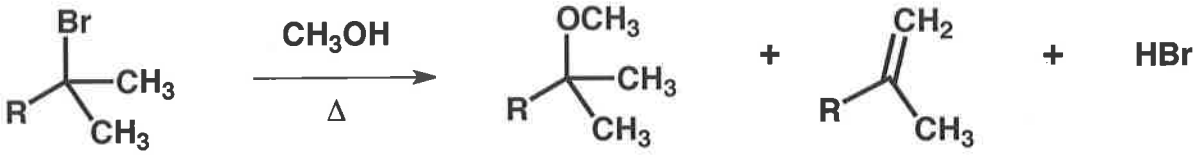


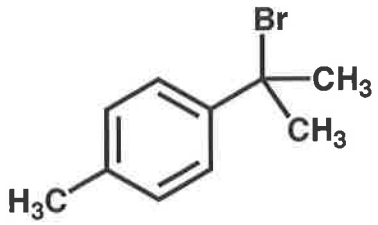
+2 for each correct symbol

(-1 for incorrect symbols; no score below 0 for any structure)

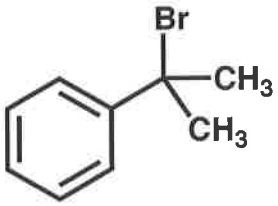
Name _____

8. (8 points) Each of the four molecules shown below (A-D) undergoes the reaction shown. Rank these four molecules in terms of increasing reaction rate, with the molecule expected to react MOST rapidly on the RIGHT.

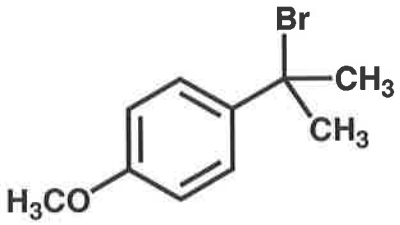




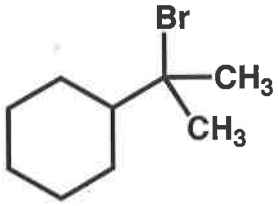
A



B



C



D

INCREASING reaction rate to the RIGHT:

D < B < A < C

(+2) (+2)

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

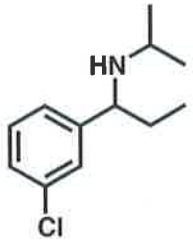
+8 for all 4 correct

Name _____

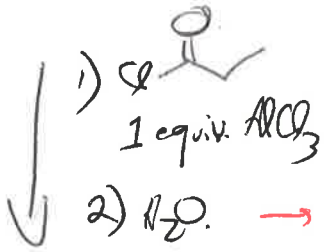
9. (35 points)

(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 = 

(+5)

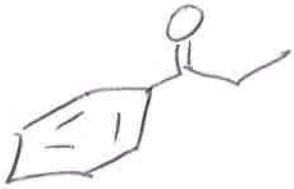


-1 for catalytic $AlCl_3$

-2 for no H_2O

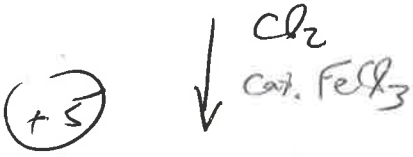
-2 for e⁻ poor FC on nitro route

-5 for no $AlCl_3$



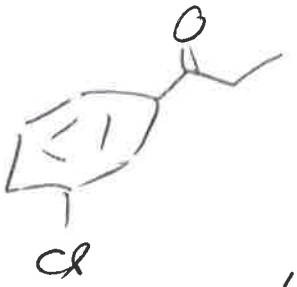
-1 for slight error in reagents

(+5)

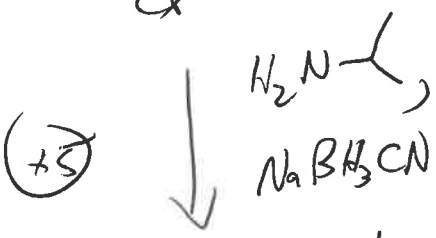


Nitration / reduction / diazonium / CuCl instead of chlorination

2/5

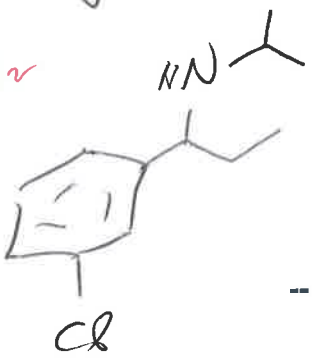


(+5)



2/5 for carbonyl reduction / leaving group / S_N2

3/5 Raney Ni, H_2



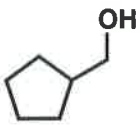
2/5 for imine formation wrong reductant

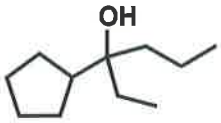
-- cont. on next page --

Name _____

9. (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.

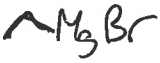
Starting material = 

Target = 

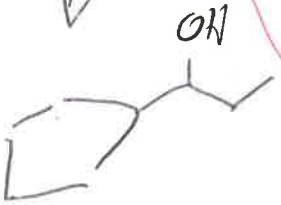
(racemic)

+5 PCC

[RLi ok]

+5 1) 

2) $H_3O^{\oplus}$



+5 $K_2Cr_2O_7$, H_2SO_4

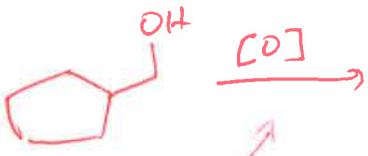
[other ox. ok]

+5 1) 

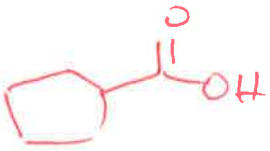
2) $H_3O^{\oplus}$

+3 for cuprate

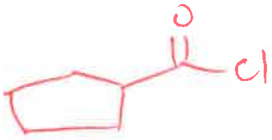
Alternative



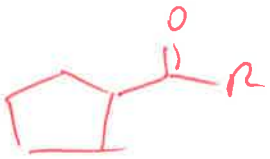
MnO_2 gets O/S



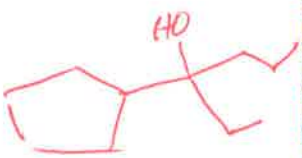
$SOCl_2$



R_2CuLi



R-L



0/10

2 points for adding organometallics to esters, ~~esters~~

or Grignard to acid chloride