Hour Exam #2
Chemistry 345
Professor Gellman
26 March 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.

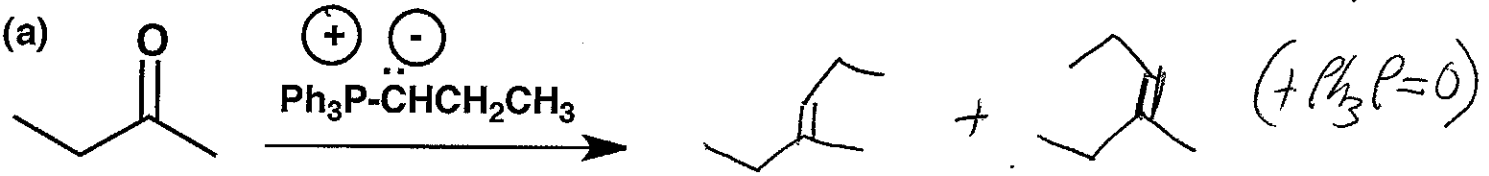
(ii) Print your name on each page.

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

[Not required]

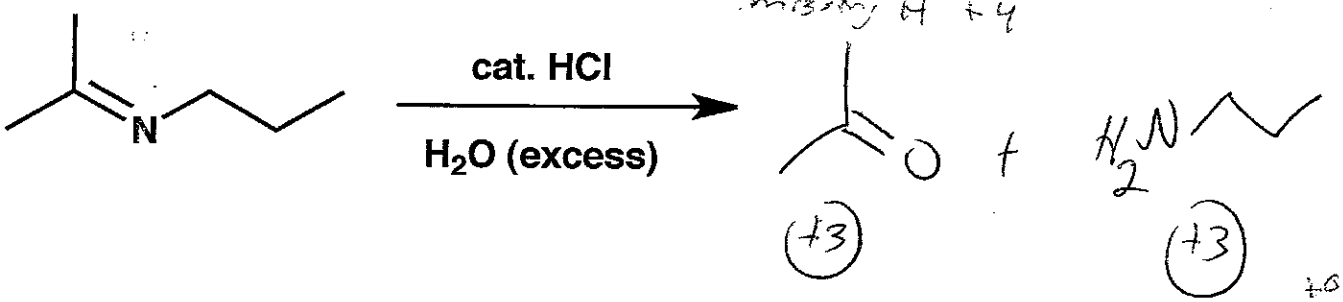
1. (20 points) Show the product(s) expected from the reactions indicated below.

(a)



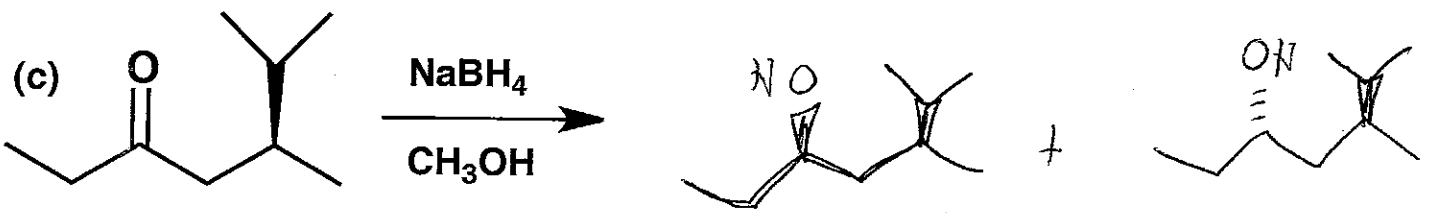
+5 for one; +7 for both
(+4 for alkene w/unclear geometry)

(b)



extra carbon +3
missing carbon +3
missing H +4

(c)



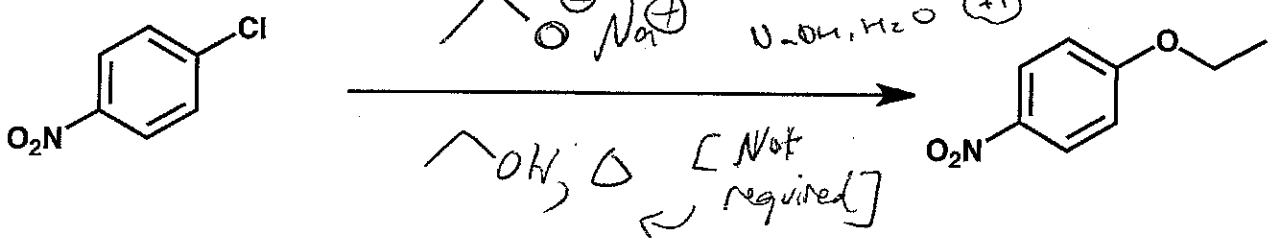
(single enantiomer)

+5 for one; +7 for both
(+3 for redn product w/o stereochem)

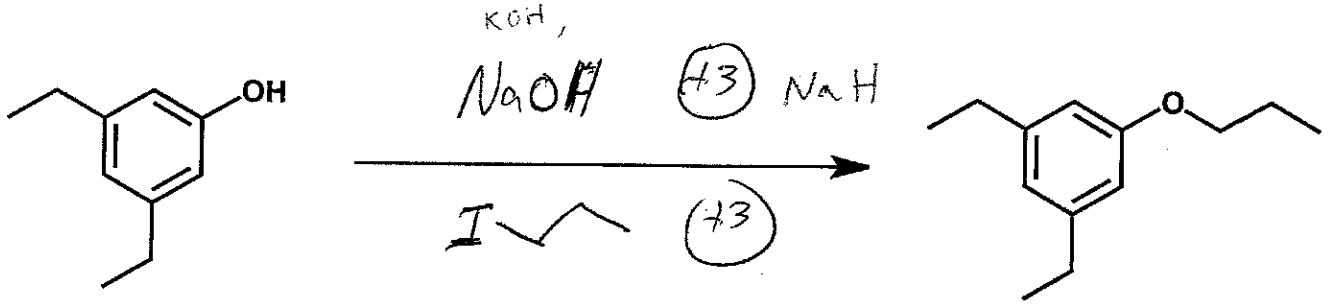
Name _____

2. (20 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.

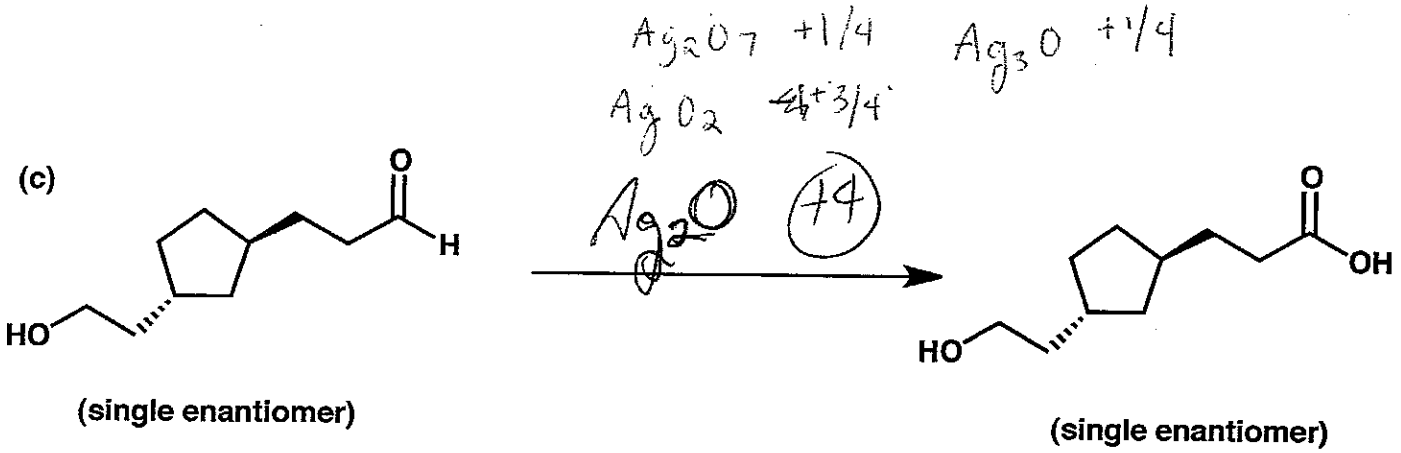
(a)



(b)



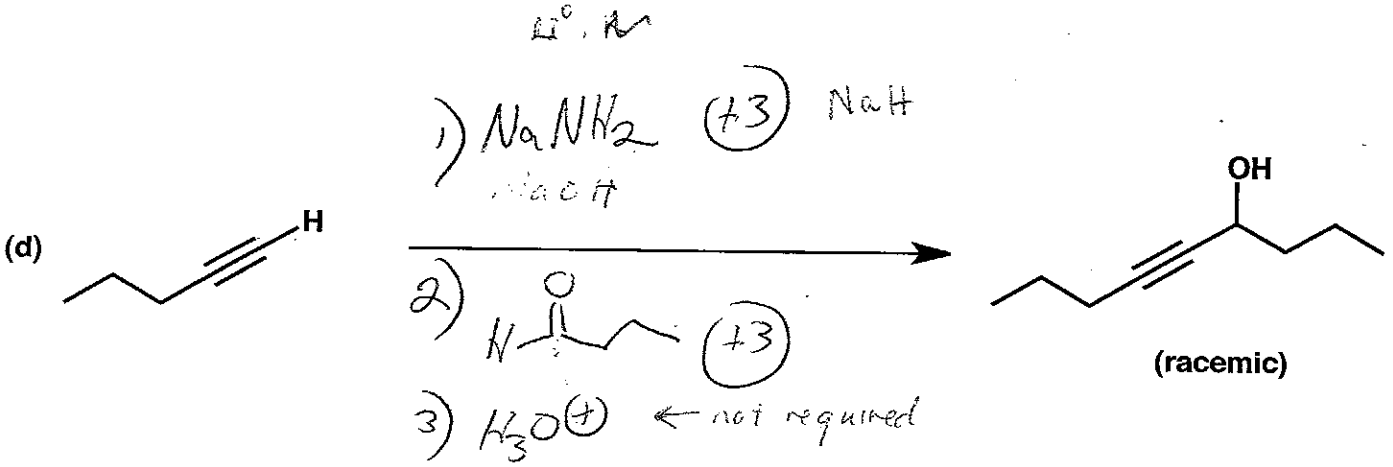
(c)



(single enantiomer)

(single enantiomer)

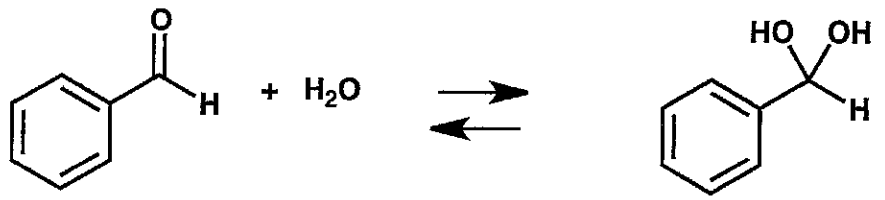
(d)



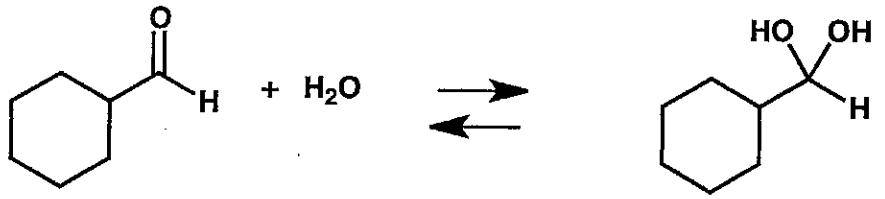
(racemic)

Name _____

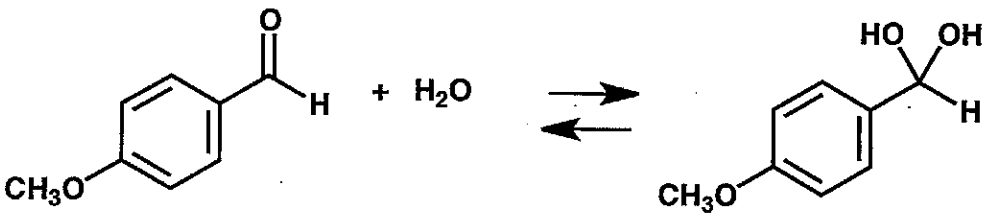
3. (8 points) Rank the four equilibria below (A, B, C and D) in terms of the extent to which the RIGHT side will be favored, from least to most.



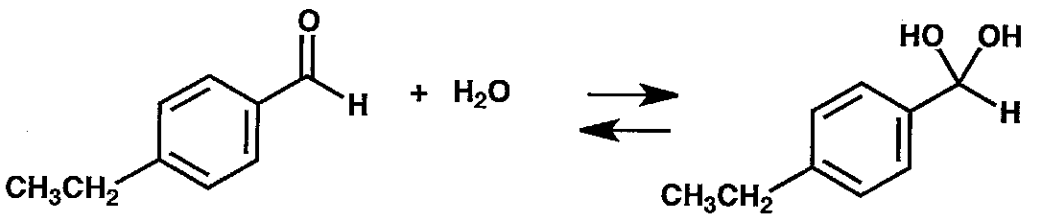
eq. A



eq. B



eq. C



eq. D

+8

INCREASING tendency to lie to the RIGHT:

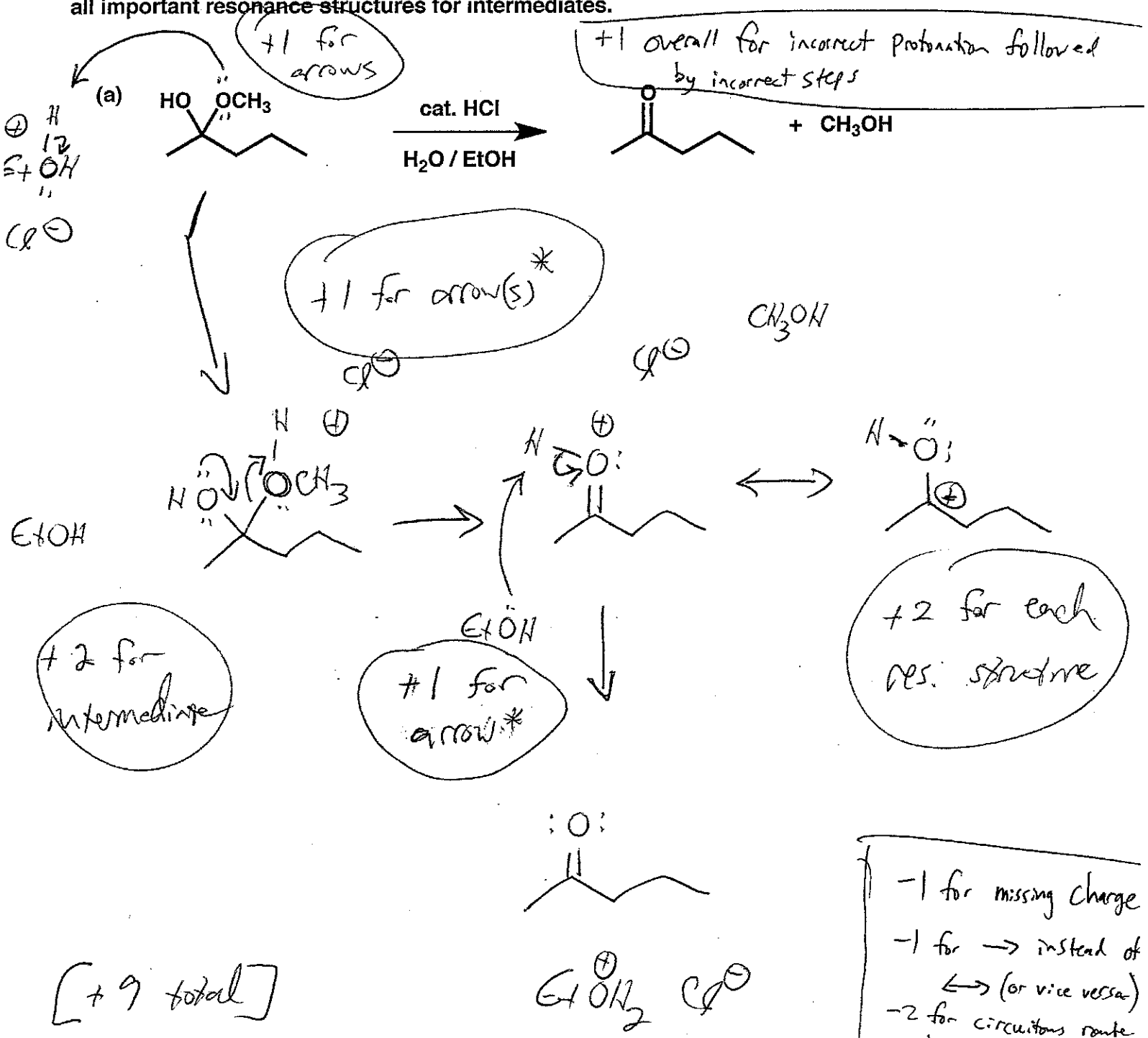
C _____ < D _____ < A _____ < B _____

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

Partial: C 2 leftmost = +2
B 2 rightmost = +2

Name _____

4. (17 points) Provide a mechanism (curved arrows) for each reaction shown below. Draw all important resonance structures for intermediates.



* Correct arrow(s) can be drawn for any proper res. structure. # of arrows may vary w/res. struct chosen.

(cont. on next page)

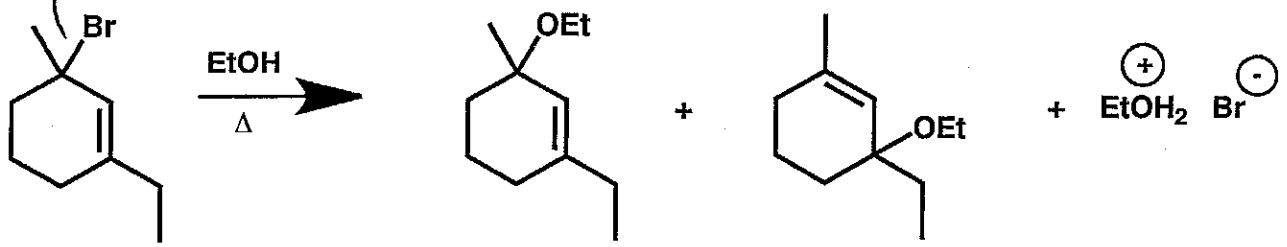
Name _____

4. (cont.)

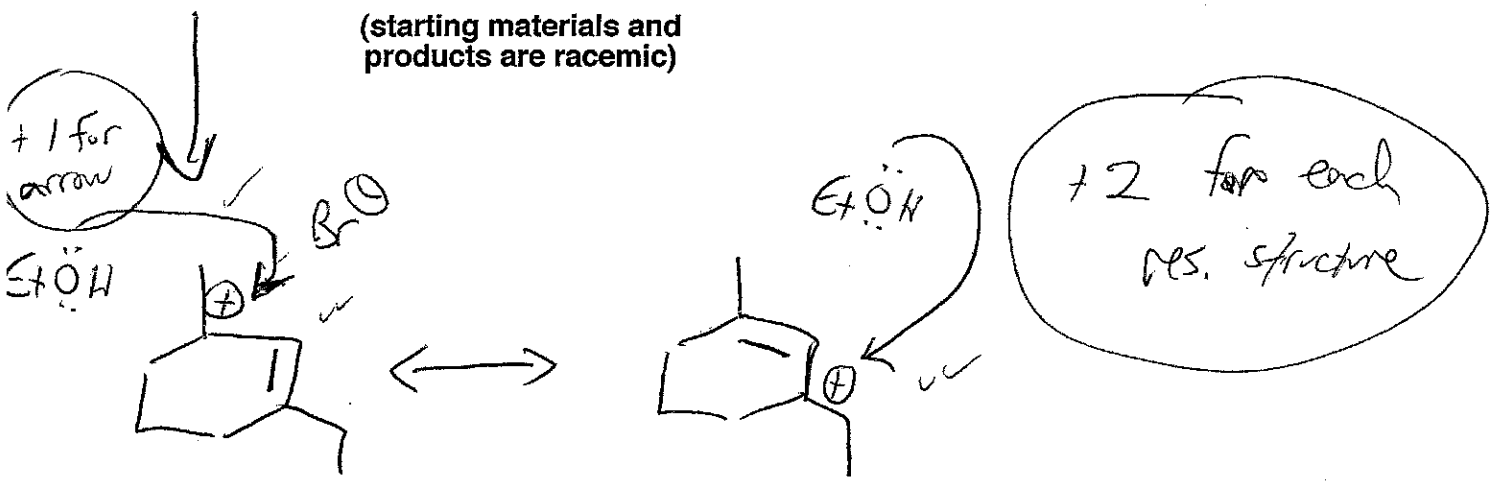
+1 for arrow

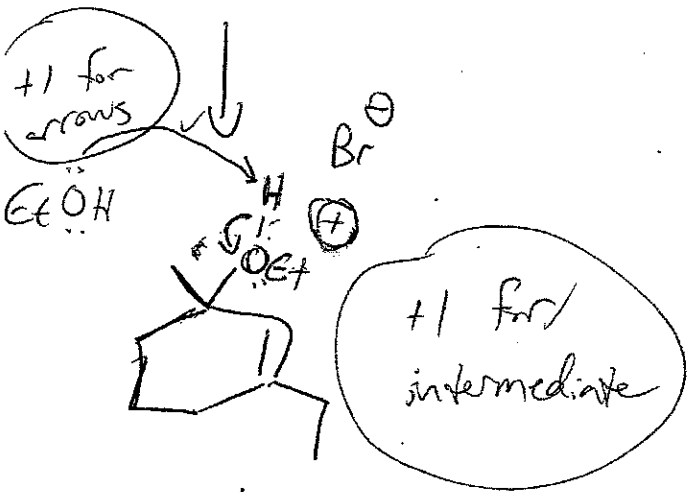
− 2 FOR $^{\ominus}OEt$ MECHANISM

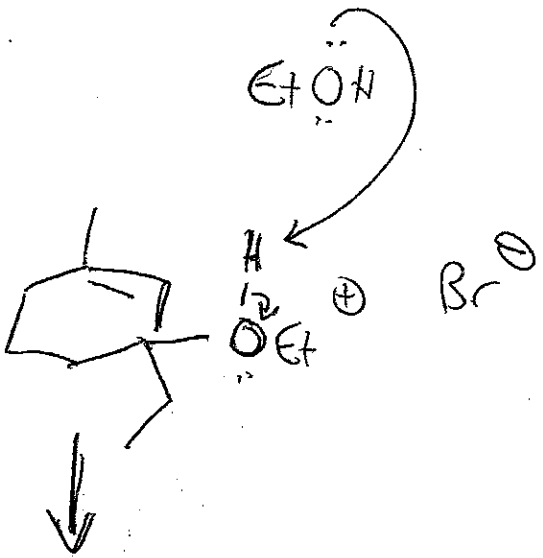
(b)



(starting materials and products are racemic)

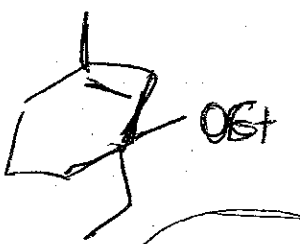






[Note: need only one correct mech after res. structures.]

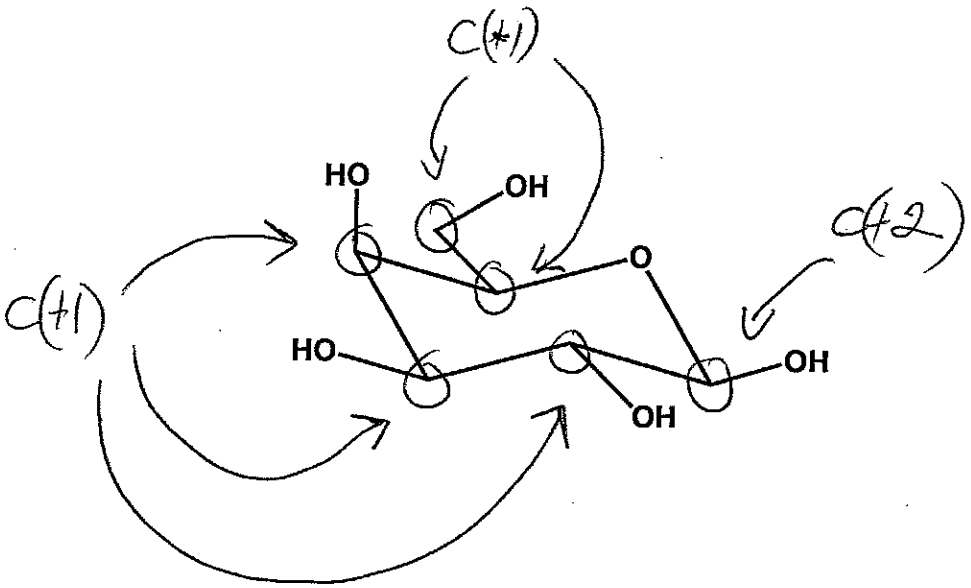
+ $EtOH_2$ $Br^{\ominus}$



[+8 total]

Name _____

5. (6 points) Shown below is one of the naturally occurring forms of the carbohydrate designated galactose. CIRCLE each carbon atom, and next to each circle indicate the carbon atom's oxidation state, as defined in lecture.

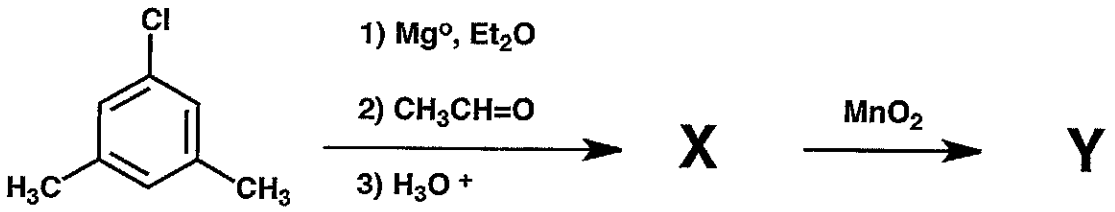


+1 for each correct

carbon ox. state

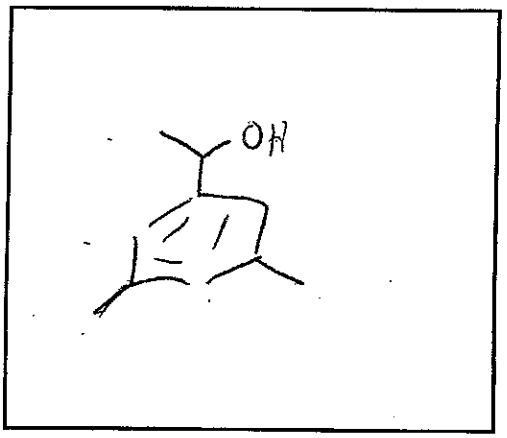
Name _____

6. (14 points) Show the structures of molecules X and Y in the appropriate boxes. The structures you propose should be consistent with the reactions shown and the spectroscopic data provided.



+7

X =



Partial spectroscopic data:

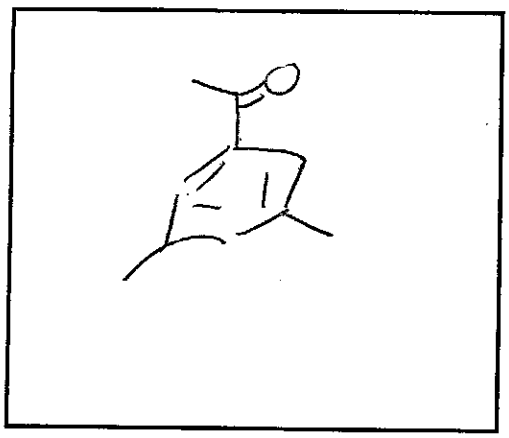
IR: Strong band in range 3250-3350 cm^{-1}

^{13}C NMR: Seven resonances

^{1}H NMR: Six resonances, one of which is lost upon shaking with D_2O.

+7

Y =



Partial spectroscopic data:

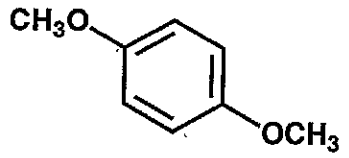
IR: Strong band in range 1680-1690 cm^{-1}

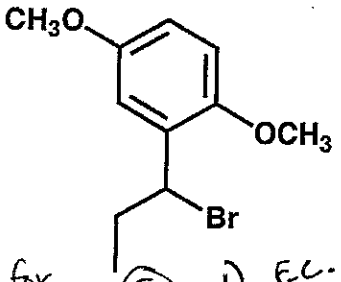
^{13}C NMR: Seven resonances

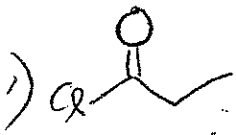
^{1}H NMR: Four resonances; none is lost upon shaking with D_2O.

Name _____

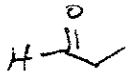
7. (15 points) Propose an efficient synthetic route from the indicated starting material to the target. You may use any other starting materials and reagents.

Starting material = 

Target = 

(+4) 1) 
1 equiv. $AlCl_3$

(+1) 2) H_2O

~~3/5~~ 3/5 if 

or:

4/5 for no H_2O (5) 1) F.C. acylation

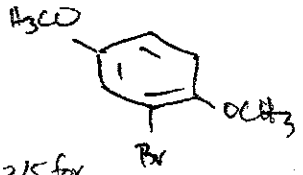
(5) 2) Reduction of ketone

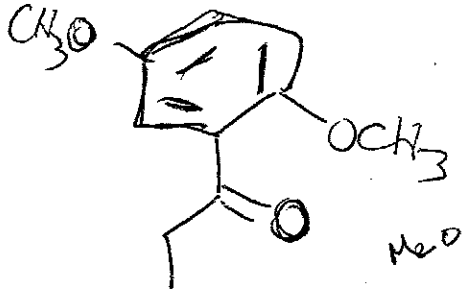
(5) 3) Bromination of alcohol

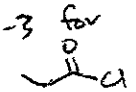
Also:


-3 if no L.A.

Br_2, $FeBr_3$ (5)

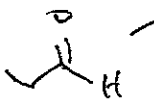


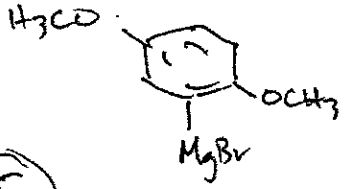


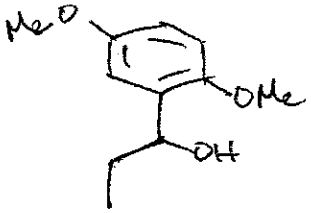
-3 for 

(5) 2/5 for vinyl Mg

Mg^0







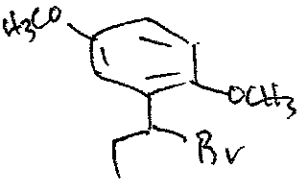
(+5) Zn/Hg, ~~HCl~~

or

H_2NNH_2, KOH

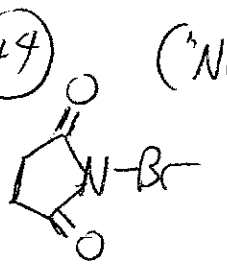
HBr (5)

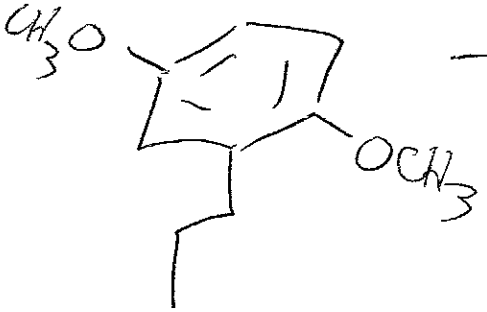
or PBr_3



< -1 pt overall for unnecessary (not harmful) steps

(+4) ("NBS")





CCl_4, peroxides, Δ or $h\nu$ (+1)