Hour Exam #3 (PM)
Chemistry 343
Professor Gellman
3 December 2012

Last Name Answers

First Name Key

General Instructions:

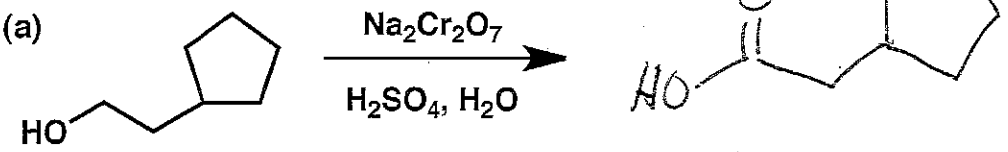
(i) Use scratch paper at the back of the exam to work out answers; final answers must be recorded at the proper place on the exam itself for credit. Models are allowed.

(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.

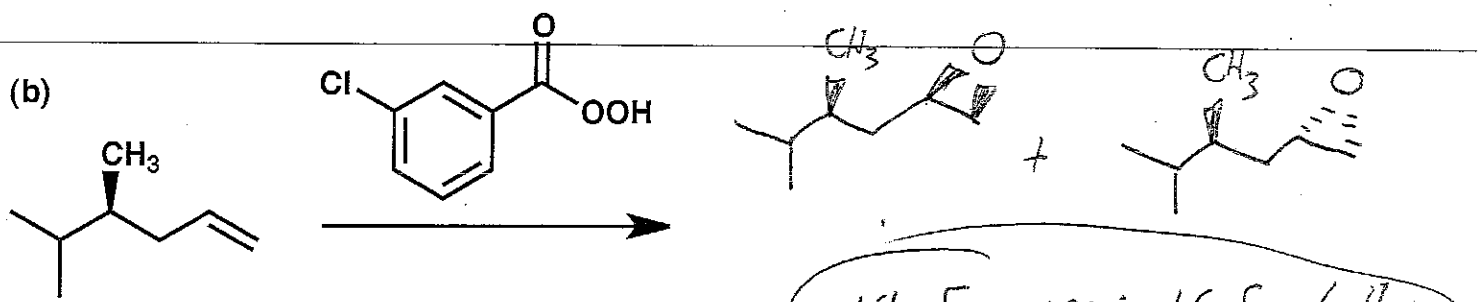
1. (16 points) Show the major product(s) expected from the reactions below.

(a)



(+5)
+2 for extra carbon
+0 for aldehyde

(b)

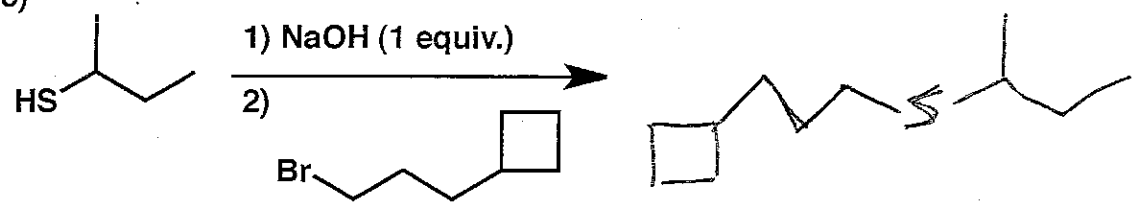


(single enantiomer)

+4 for one; +6 for both

(+2 for no or incorrect stereochem
+ -2 missing carbon

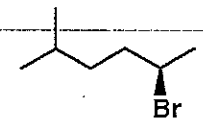
(c)



(+5)
~~+2~~ +3 for extra carbon or loss of carbon

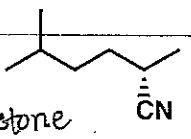
Name PM

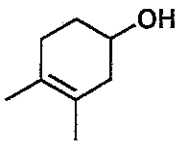
2. (20 points) Show the reagents required to convert the starting molecule to the indicated product. If necessary, be sure to differentiate clearly between distinct steps, by using "1)", "2)", etc. over the arrow.

(a) 

(+4) NaCN (−1 ^-CN, −2 HCN)

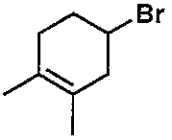
(+1) DMSO (DMF ok) THF, pyridine — −1 acetone

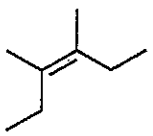


(b) 

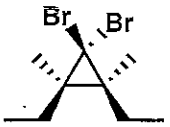
(+4) PBr_3 (−1 TsCl/NaBr)

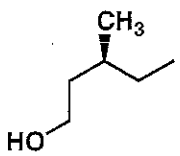
(No credit for "HBr")



(c) 

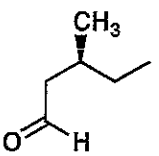
(+3) $HCBr_3$, NaOtBu (+3)



(d) 

(+4) PCC

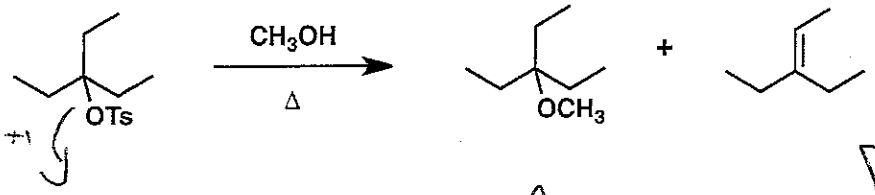
(+1) CH_2Cl_2, pyridine



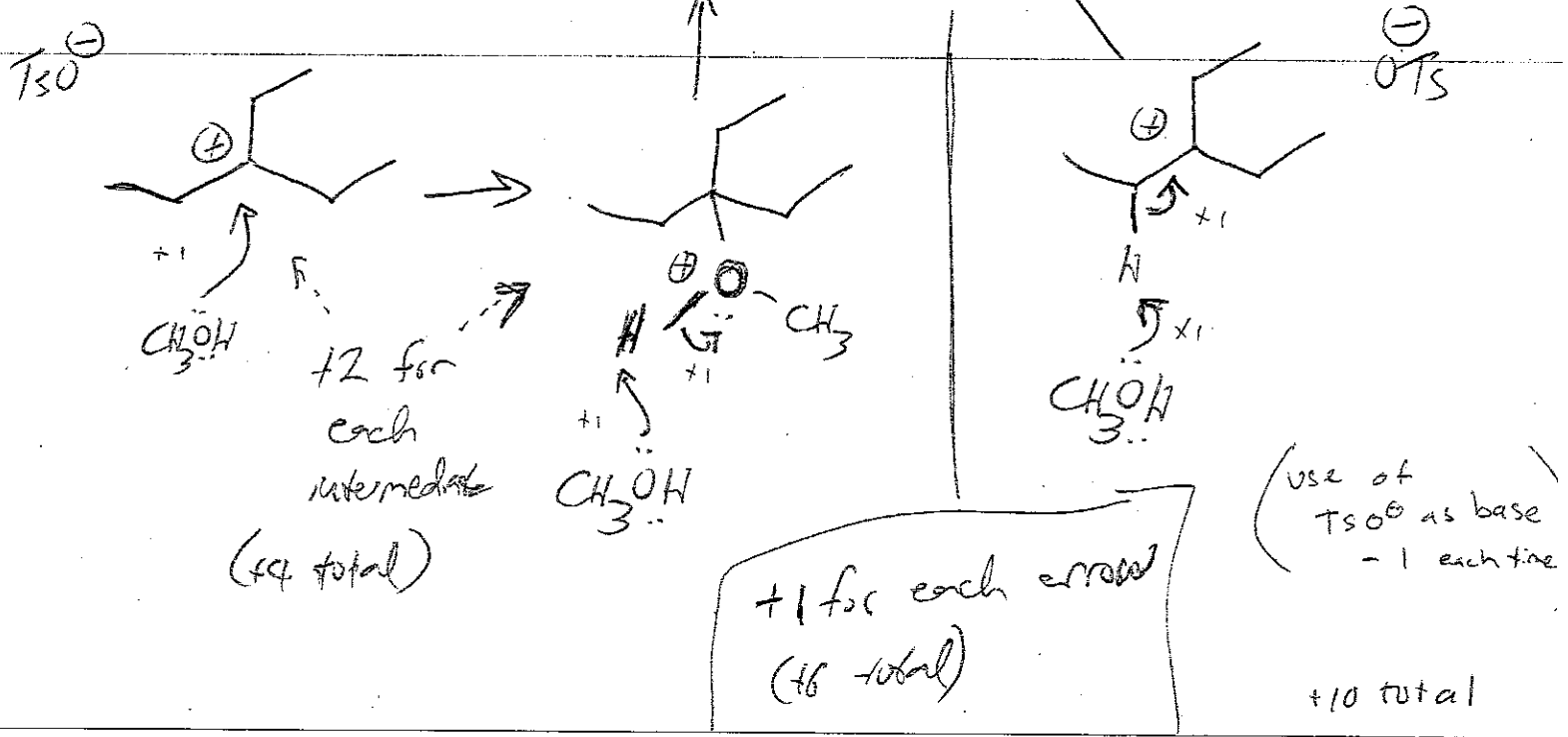
Name PM

3. (22 points)

(a) Provide a mechanism (curved arrows) that accounts for both of the products shown below.

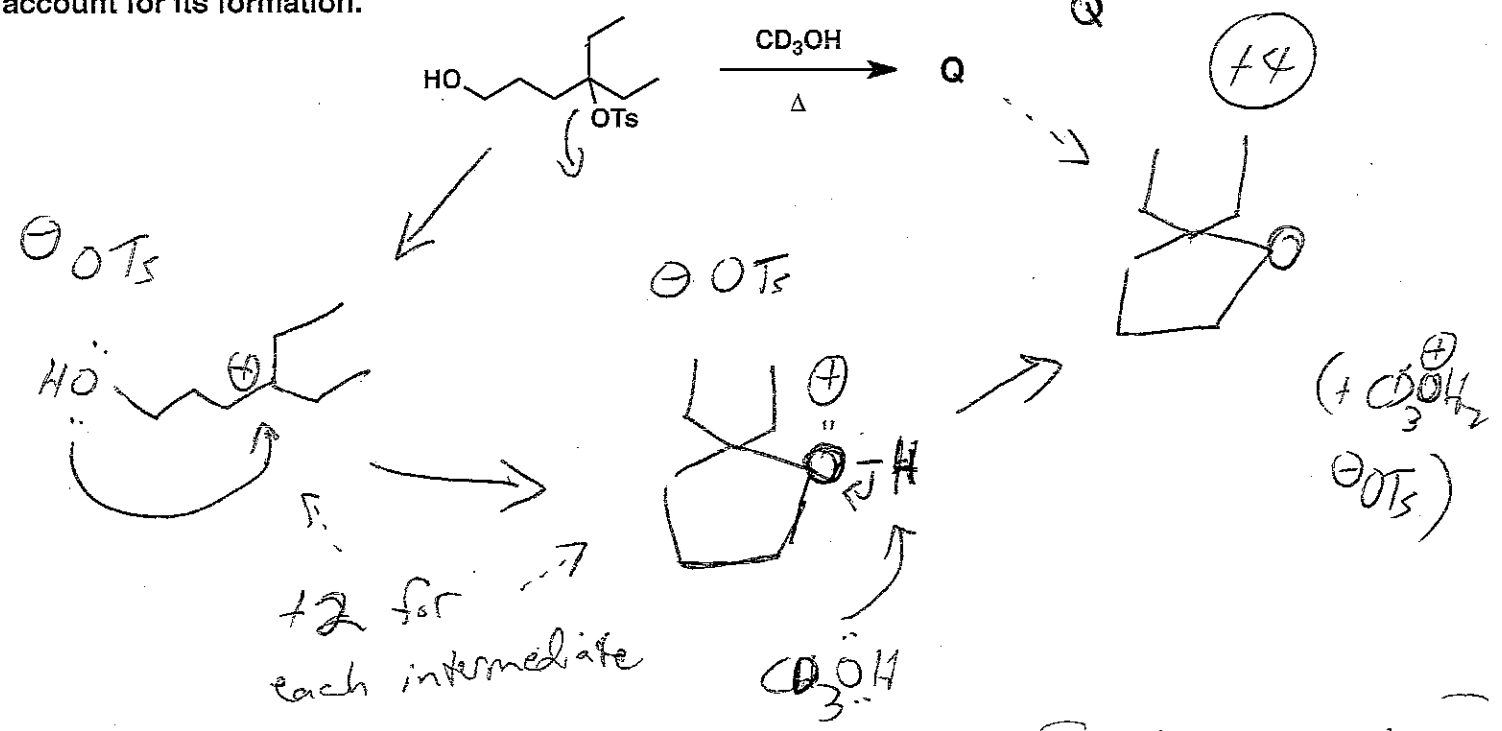


Not required



+10 total

(b) The reaction below produces only a single product, Q, which does not contain deuterium and does not react further when exposed to H_2 and Pd/C. Show the structure of Q and a mechanism to account for its formation.

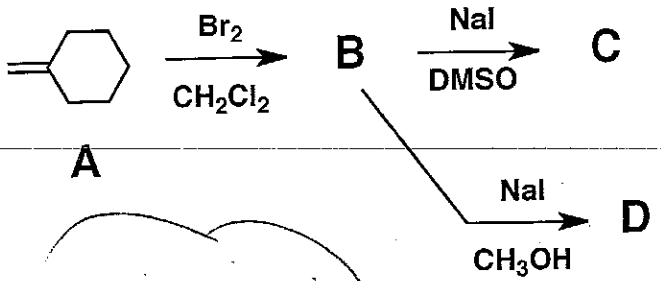


+12 total

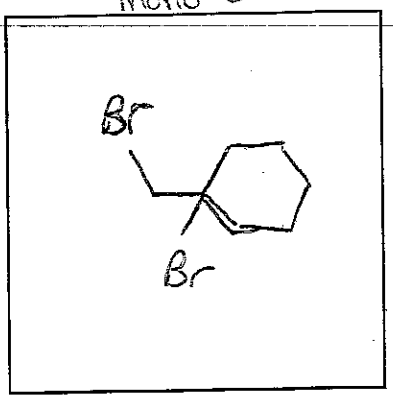
Name PM

4. (15 points) When alkene A is allowed to react with molecular bromine in methylene chloride, molecule B is formed. B reacts with sodium iodide in DMSO to produce only one product, C. In contrast, when B reacts with sodium iodide in methanol with heating, several products are generated. C is not among these products, but D, an isomer of C, *is* formed during the reaction in methanol.

Provide structures of B-D in the boxes below.

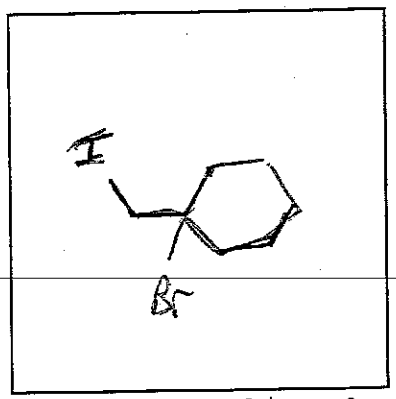


B =



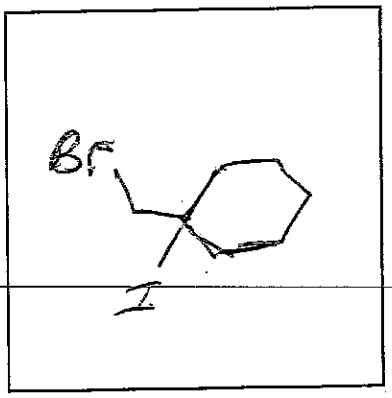
+5 each

C =

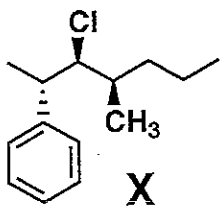


swap C+D → +2 each

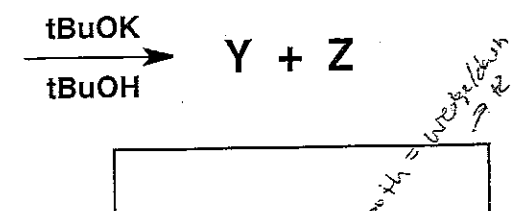
D =



5. (10 points) Molecule X is a single enantiomer. The reaction shown below generates two products, Y and Z. Provide structures of Y and Z in the boxes below.

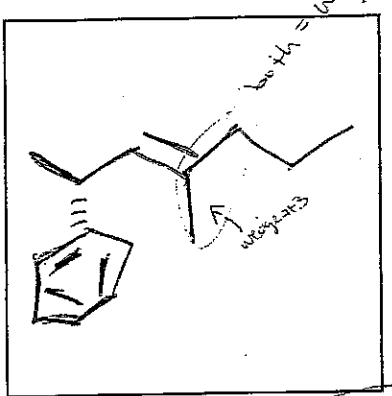


X

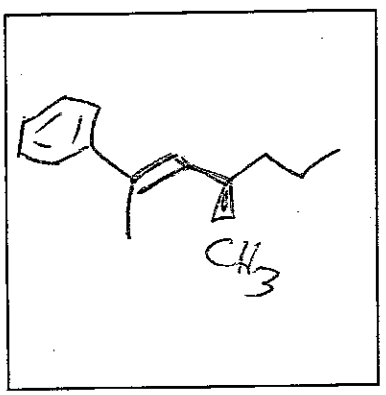


Y + Z

Y =



Z =



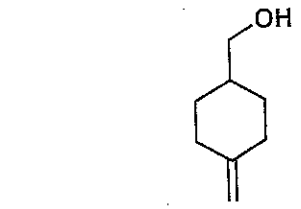
+5 each

(+2 for no or incorrect stereochem)

Name PM

6. (17 points) Suggest a synthetic route (i.e., a specific sequence of reactions) that would be expected to produce the "target" molecule from the indicated starting material. You may use any other molecules and reagents in the proposed route. Try to reach the target with the fewest possible reactions, and try to choose reactions that are as selective as possible for one product (rather than a mixture of products).

Starting Material

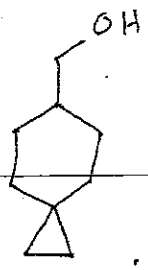


+3

+3

CH_2I_2

Zn-Cu



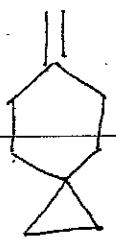
PBr_3

+3

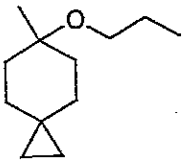
t-BuOK

t-BuOH

+2



Target



+3

1) $Hg(OAc)_2$, HO

2) $NaBH_4$

+3

H_2SO_4, H_2O

ok

$TsCl$, pyridine

or

$SOCl_2$, pyridine

ok

(or HBr, H_2O)