00336

Hour Exam #2
Chemistry 343
Professor Gellman
2 November 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.

(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.

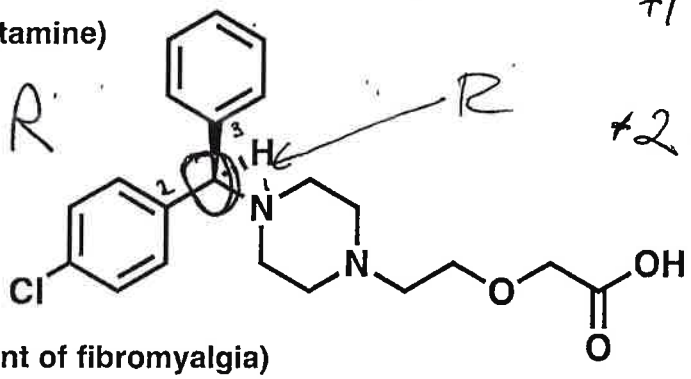
1. (13 points) Shown below are the structures of two drug molecules. In each case, CIRCLE each of the chiral centers, and indicate configuration (R vs. S) for each chiral center. Be sure to answer the question at the bottom.

+1 for each correct circle

+2 for each correct R/S

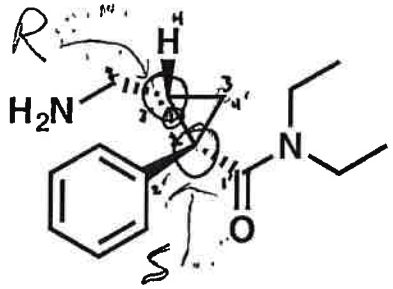
(a) Cetrizine (an antihistamine)

+3

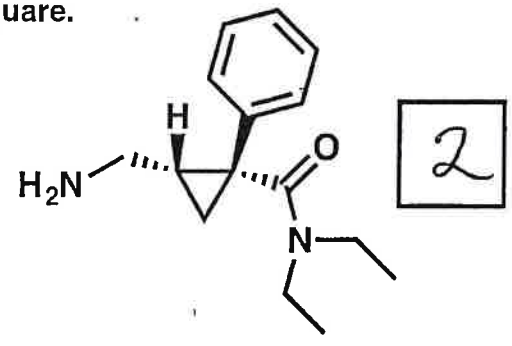


(b) Milnacipran (treatment of fibromyalgia)

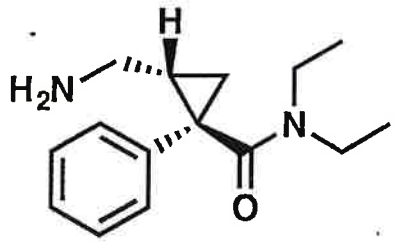
+6



(c) For each structure below, one of the three statements about optical activity given is correct. In each case, write the numeral corresponding to the correct statement in the square.



2



3

+4

(1) The specific rotation will be identical to that of the molecule shown in part (b).

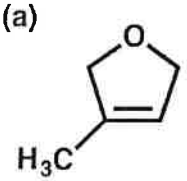
(2) The specific rotation will have the same absolute value but the opposite sign relative to that of the molecule shown in part (b).

(3) No prediction about the specific rotation can be made.

Name _____

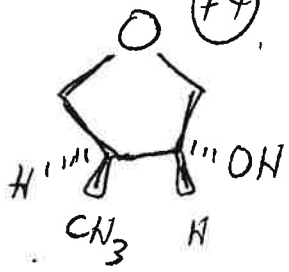
2. (24 points) Show the major product(s) expected from each reaction below. −2 for syn & anti addition product

(a)



1) BH_3 (0.33 equiv.), THF

2) H_2O_2, NaOH, H_2O

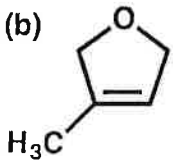


(+4) (+2) (racemic)

+1 if markovnikov product

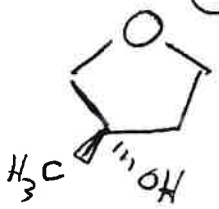
+1 if no/incorrect stereochem

(b)



1) $Hg(OAc)_2$, H_2O, THF

2) $NaBH_4$



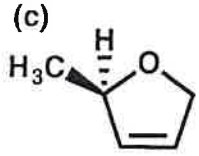
(+4) (+2) (racemic)

+1 $Hg(OAc)_2$ there and syn w/ OH group

+2 if $Hg(OAc)_2$ is still there

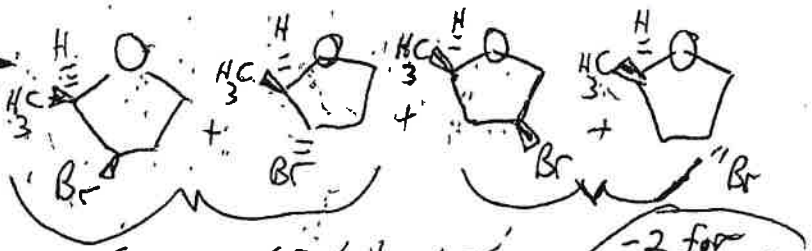
+1 if anti markovnikov product

(c)



HBr

Benzoyl peroxide



(single enantiomer)

+0 halohydrin for ~~boto~~ formation

+2 if no stereochem

+4 for one; +6 for both

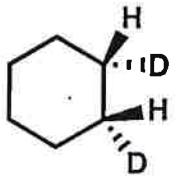
−2 for "racemic"

3. (12 points) Show the reagents required to convert the starting molecule to the indicated product. If necessary, differentiate between or among distinct steps by using "1)", "2)", etc.

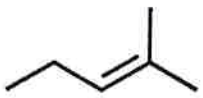
(a)

D_2 (+3)

Pd/C (+3)

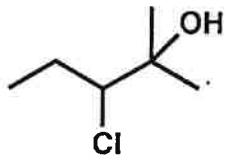


(b)



Cl_2 (+3)

H_2O (+3)



(±)

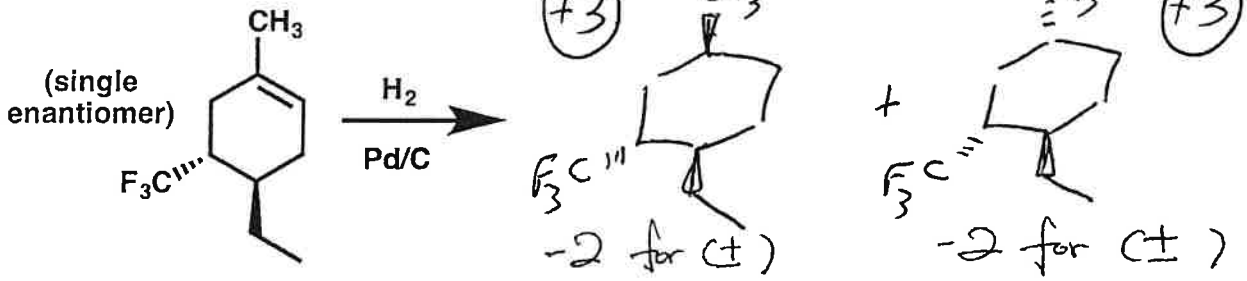
+4 max for multiple steps

Cl_2 / H_2O, CH_2Cl_2 → +3

Name _____

4. (22 points)

(a) Two products are formed in the reaction indicated below. Draw the structures of those products after the arrow.

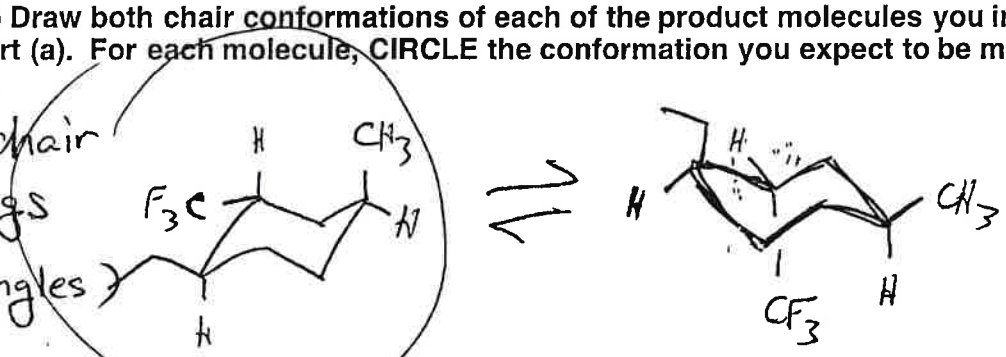


(b) On the line below, indicate the relationship between the two product molecules. Be as specific as possible.

Diastereomers (+2)

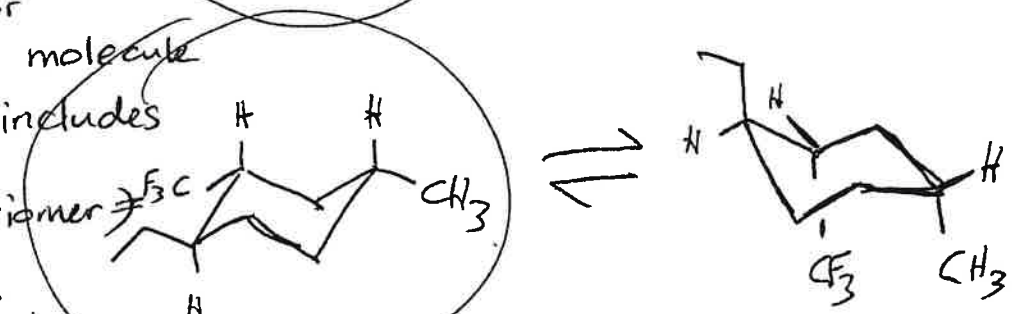
(c) Draw both chair conformations of each of the product molecules you indicated in part (a). For each molecule, CIRCLE the conformation you expect to be more stable.

+0 for wrong chair drawings (wrong bond angles)



+2 for each correct chair

+0 for wrong molecule (this includes the enantiomer of each product molecule)

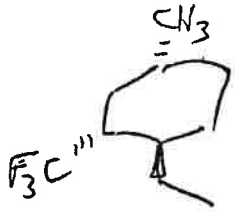


+2 for each correct circle

[+12 total]

Not considered unless chairs are correct

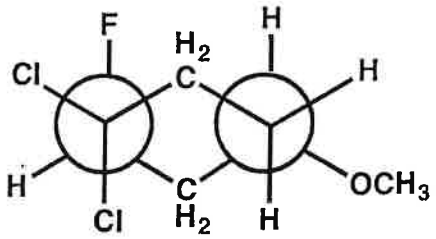
(d) Of the products generated in the reaction above, which molecule should be most stable (i.e., which should release least heat upon combustion)? Answer this question by redrawing below the appropriate molecule.



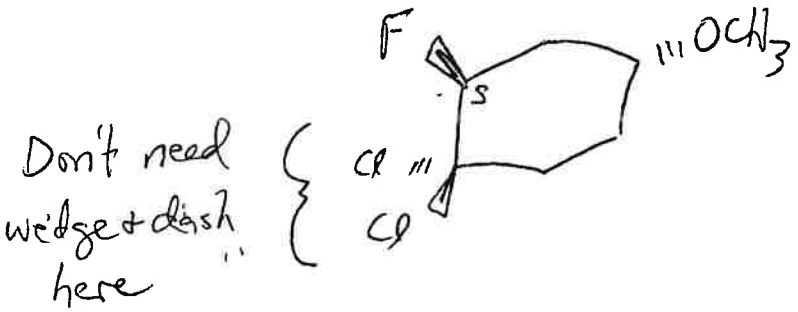
(+2)

Name _____

5. (10 points) Consider the Newman projection below.



(a) Provide a "hexagon" drawing for the molecule shown in the Newman projection above.

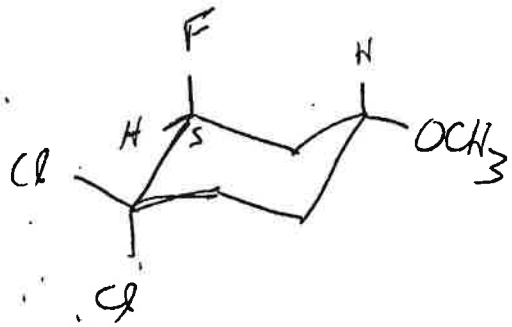


Don't need wedge + dash here

+4

no points for enantiomer

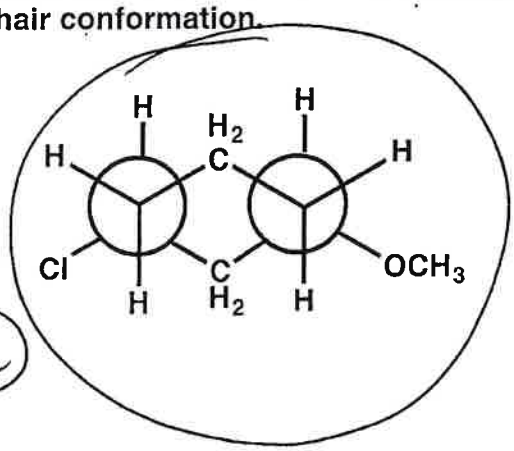
(b) Provide a "chair" drawing for the molecule shown in the Newman projection above, maintaining the conformation indicated by this Newman projection.



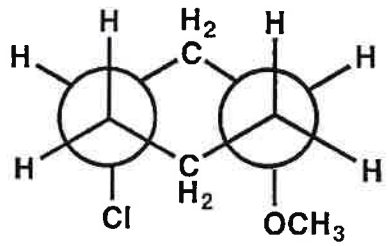
+4

no points for enantiomer

(c) Shown below are the Newman projections for the two chair forms of a substituted cyclohexane derivative. CIRCLE the Newman projection that corresponds to the more stable chair conformation.

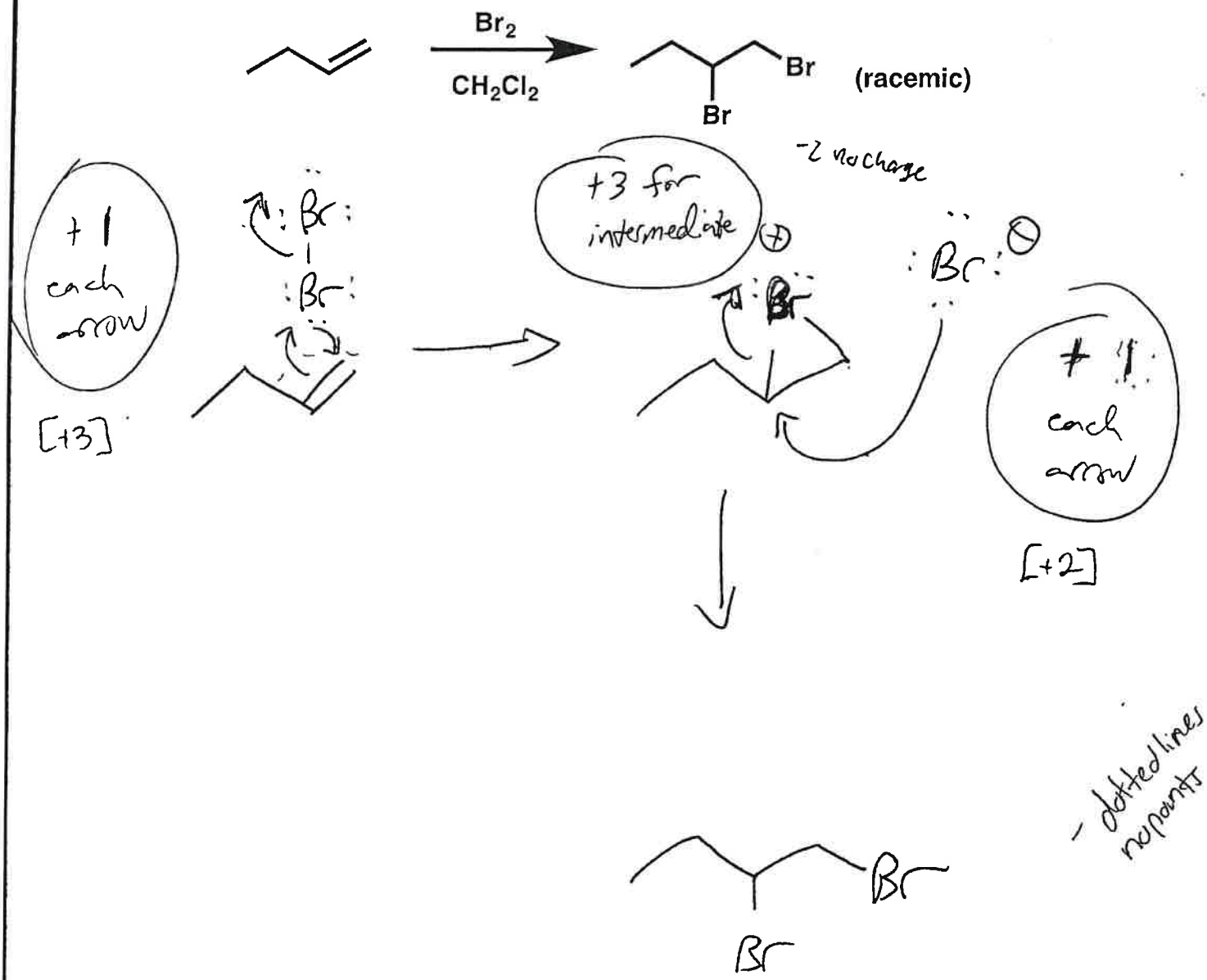


+2



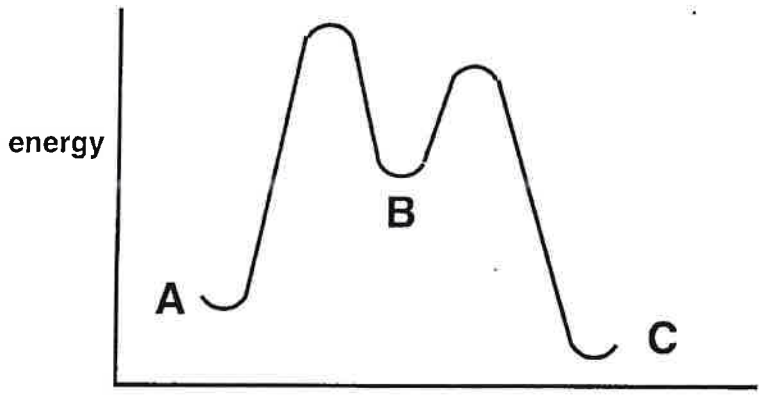
Name _____

6. (8 points) Provide a mechanism ("curved arrows") for the reaction shown below.



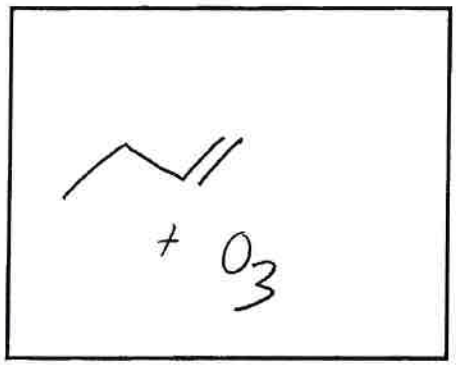
Name _____

7. (11 points) Shown below are a reaction and the energy diagram for this reaction. (Note that there is only one step in this reaction; no follow-up treatment with $(CH_3)_2S$ or H_2O_2.) Draw the structures for molecules A, B and C in the appropriate boxes below.



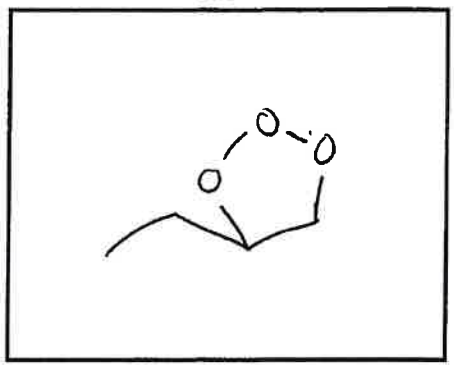
+3

A =

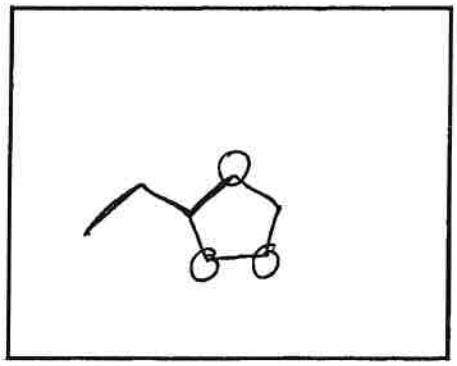


+4

B =



C =



+4