Final Exam
Chemistry 343 (AM)
Professor Gellman
17 December 2012

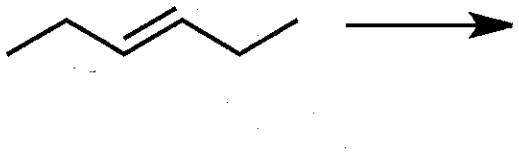
Last Name Answer

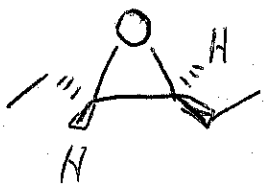
First Name Key

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 if missing)

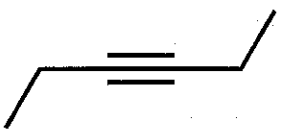
1. (39 points) Show the major product or products expected from each reaction.

(a) 

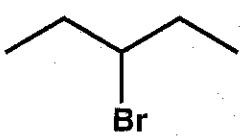


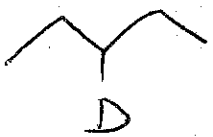
(±)

+6 (-3 if no stereochem, or incorrect)

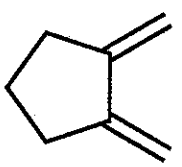
(b) 

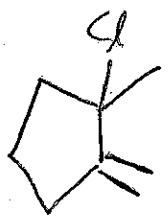
+6 (-2 if drawn twice)

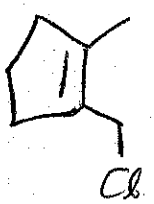
(c) 



+6

(d) 



+


Not necessary ----> (±)

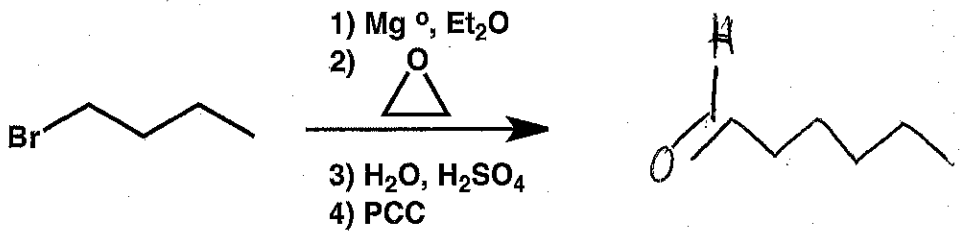
+5 for one; +9 for both

(continued on next page)

Name Key (AM)

1. (cont.)

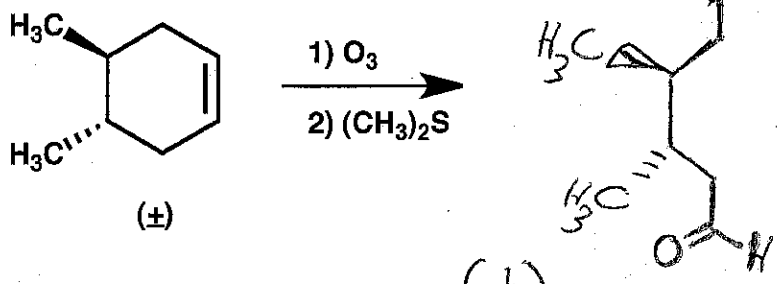
(e)



+6 (-3 for alcohol)

0 pts for wrong # of carbons

(f)

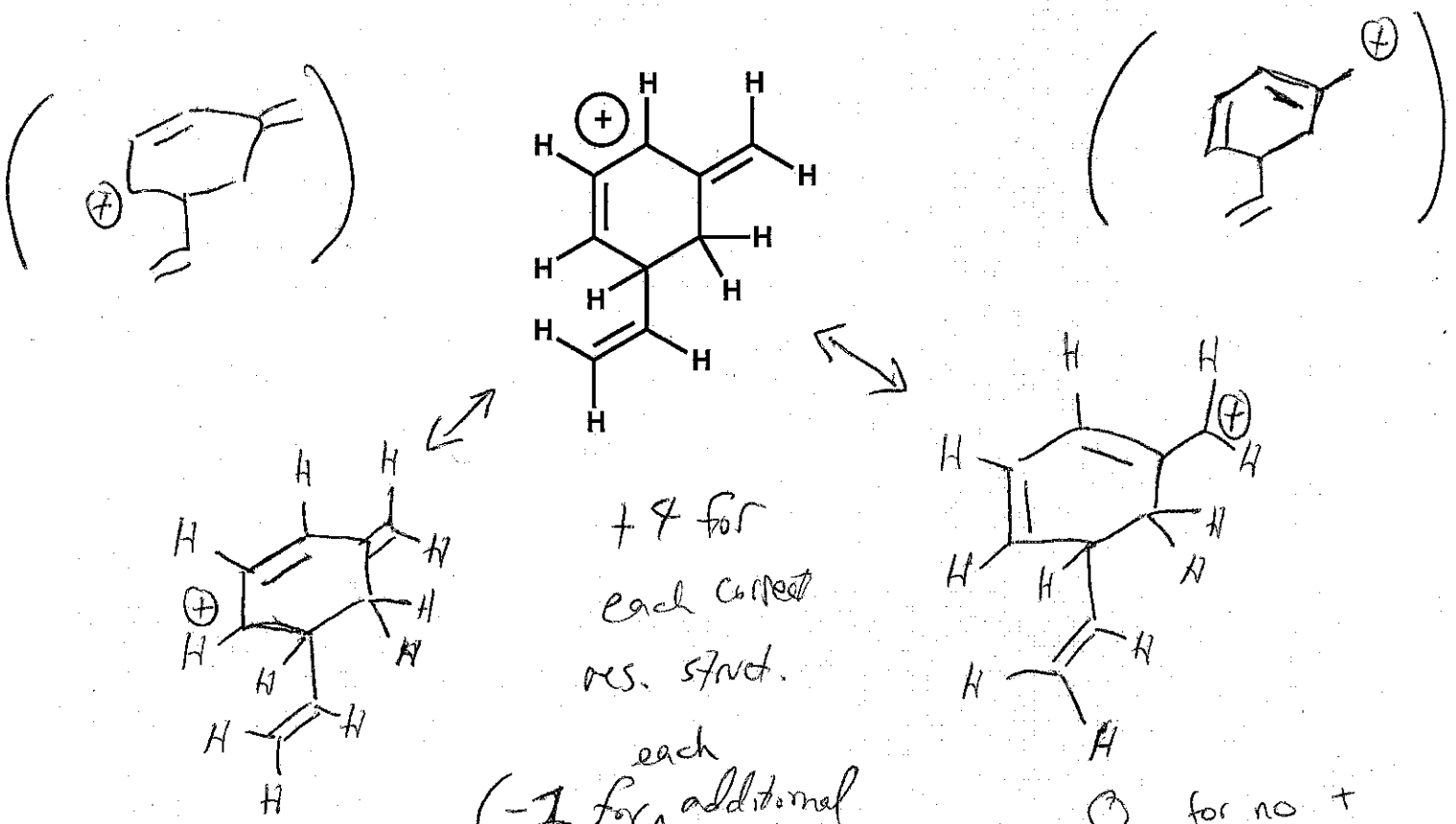


+6 -3 if no stereochem

(±)

-1 if missing

2. (8 points) Draw all of the other resonance structures for the carbocation shown below. Skeletal drawings (no H's) are acceptable, if they are correct.



+4 for each correct res. struct.

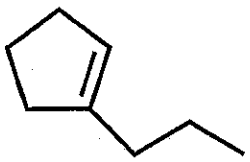
(-1 for each additional and/or incorrect structure)

0 for no + charge

Name Key (AM)

3. (23 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.

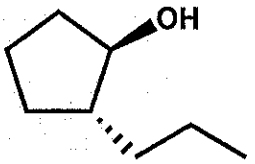
(a)



(+3) 1) BH_3, THF

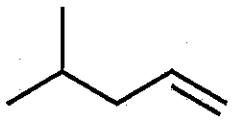
2) H_2O_2, $NaOH$, H_2O (+2) (+1)

one step: -3



(±)

(b)

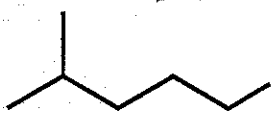


two steps: -3

(+3) HBr

(+3) peroxides (or other initiator)

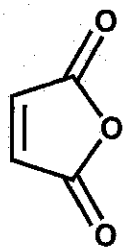
- Br_2, peroxides: +2



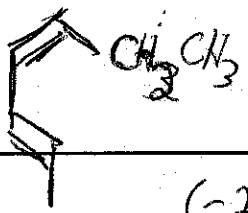
full credit

or: 1) BH_3, THF
2) $NaOH$, H_2O_2, H_2O
3) $\frac{1}{3}PBr_3$ or HBr

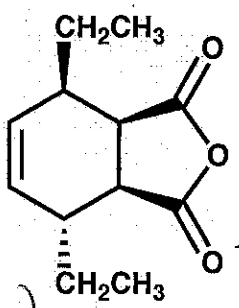
(c)



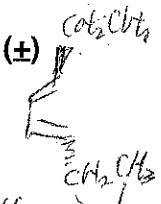
(+5)



(-2 for incorrect diene stereochem)



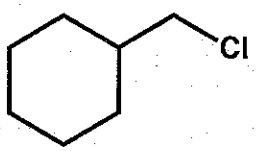
(±)



-3:

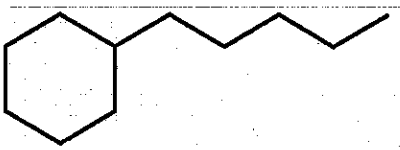
-1: ←CH_3 instead of ←CH_2CH_3

(d)



(+3) 1) $Li^{\oplus}\ ^{\ominus}:C{\equiv}CCH_2CH_3$

2) H_2, Pd/C (+3)



1) $HC{\equiv}CCH_2CH_3$ $^{\ominus}NaNH_2$ → -2

Add Mg°, ether and -3

Name Key (AM)

4. (16 points) Propose one structure each for molecules A and B (there may be more than one correct answer).

(+8) for each correct structure.

Molecule A has the formula C_8H_{10} and is not chiral.

A $\xrightarrow[\text{Pd/C}]{\text{excess } H_2}$ octane

A $\xrightarrow[\text{poisoned catalyst}]{H_2}$ no reaction

A $\xrightarrow{Br_2}$ rapid reaction, multiple products

A =

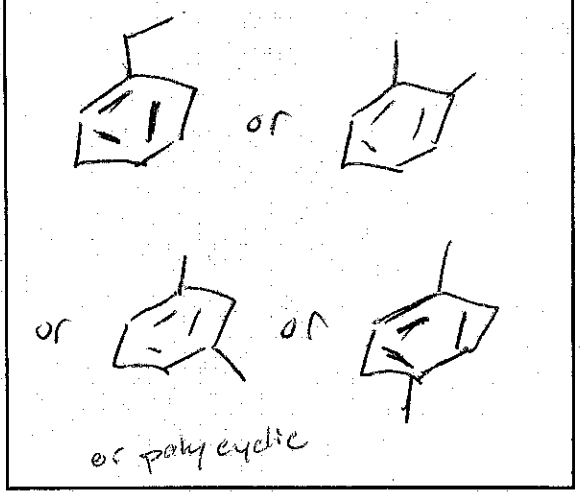
(Allene alternatives ok)

Molecule B has the formula C_8H_{10} and is not chiral.

B $\xrightarrow{Br_2}$ No reaction

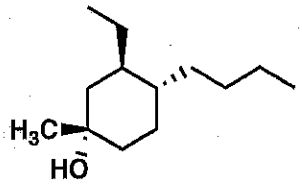
B $\xrightarrow[\text{poisoned catalyst}]{H_2}$ no reaction

B =



Name Key (AM)

5. (30 points)



D

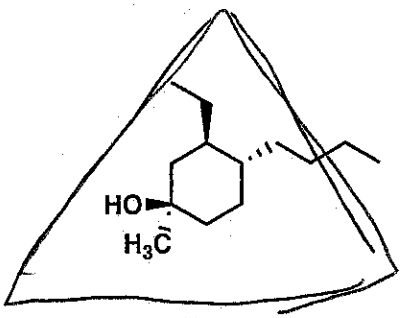
Among the structures drawn below the line, indicate isomeric relationships to the structure of molecule D, drawn above, by following the directions below. Molecule D is a single enantiomer. (Conformational differences are not relevant to this question.)

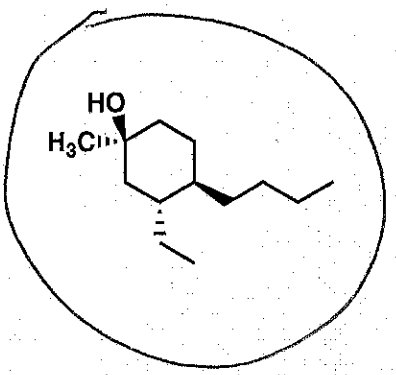
Put a CIRCLE around any structure that corresponds to D (i.e., a different drawing of the same molecule).

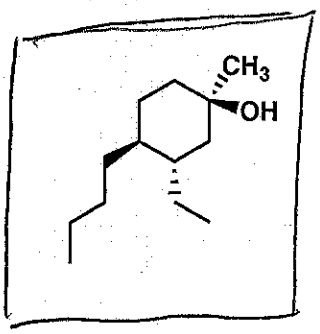
Put a SQUARE around any structure that corresponds to the ENANTIOMER of D.

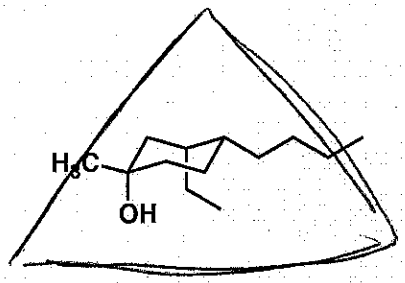
Put a TRIANGLE around any structure that corresponds to a DIASTEREOMER of D.

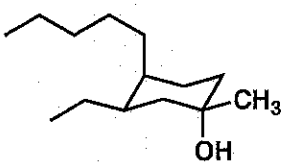
Put an X across any structure that corresponds to a CONSTITUTIONAL ISOMER of D.

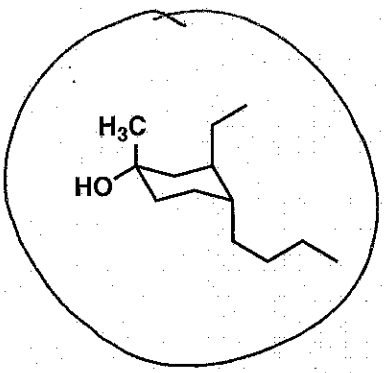










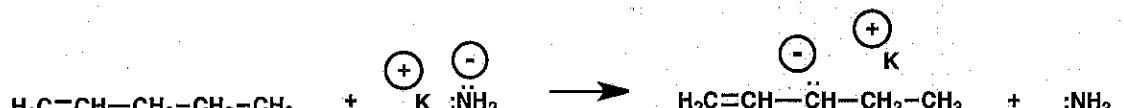


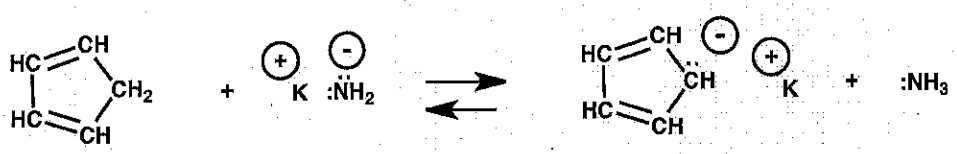
+5 for each correct symbol (or lack thereof)

Name Key (AM)

6. (5 points) For the set of equilibria shown below, indicate the order in propensity to lie to the right (most vs. intermediate vs. least), using the designations A-C.

A 

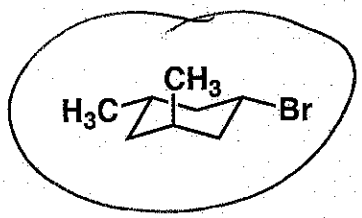
B 

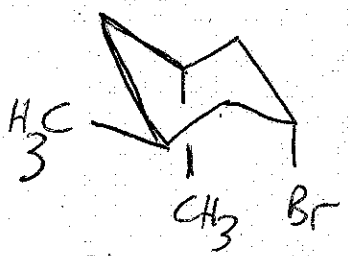
C 

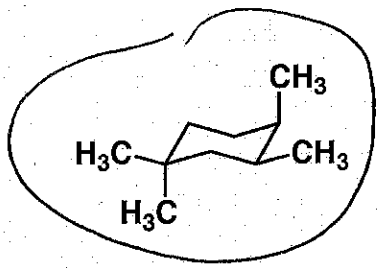
(all or none)

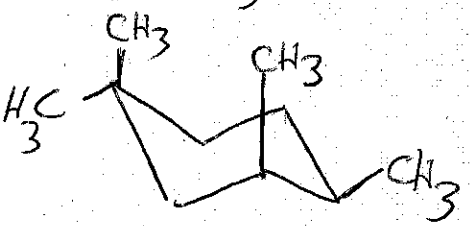
Most = C Intermediate = A Least = B

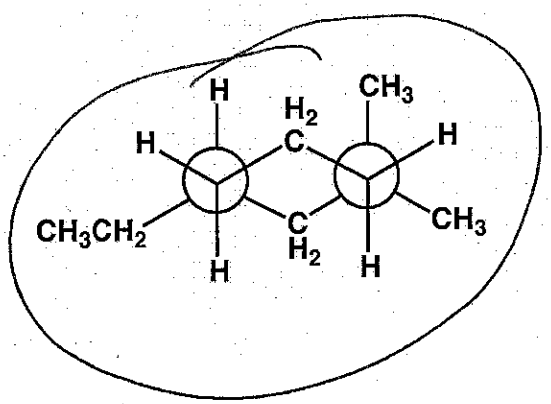
7. (18 points) For each cyclohexane conformation shown below, draw the other possible conformation (using the same drawing style as the original image), and CIRCLE the one you expect to be most stable.

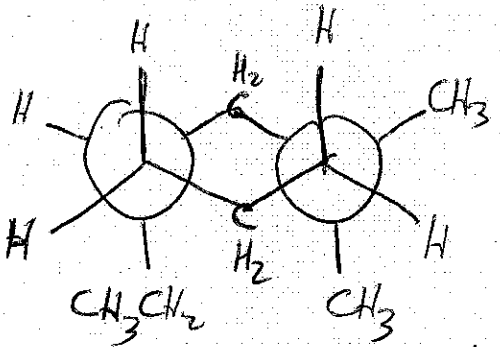
(a) 



(b) 



(c) 



+4 for each correct drawing

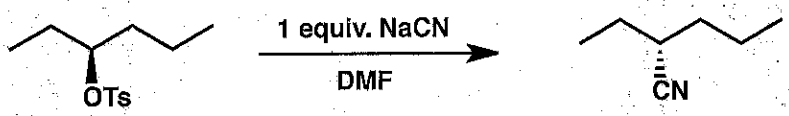
+2 for each correct circle

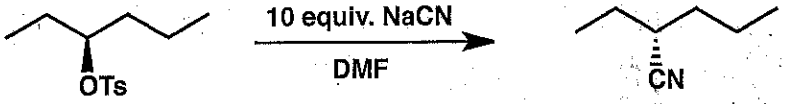
-4 if weird bond angles

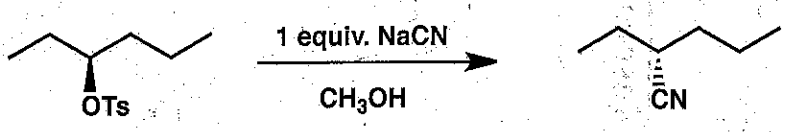
+2 if enantiomer but -4 if wrong style

Name Key (AM)

8. (5 points) For each set of reactions shown below, indicate the expected order of reaction rates (fastest vs. intermediate vs. slowest) using the designations A-C.

A 

B 

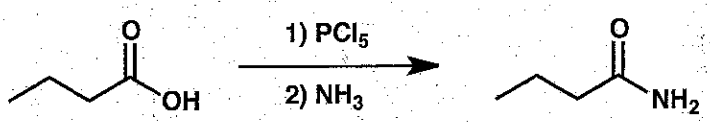
C 

(all or none)

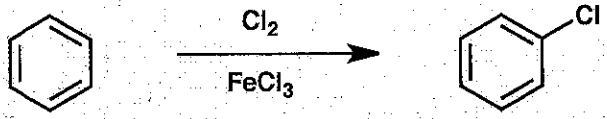
Fastest = B Intermediate = A Slowest = C

9. (6 points) Using the 'simplified' rules we discussed in class for assigning oxidation states to carbon atoms within molecules, categorize each of the reactions below as "oxidation", "reduction" or "no redox change". These categorizations should be based on the organic molecules to the left and right of the arrow; do not be concerned with any reagents. Also, do not concern yourself with the mechanism of any reaction below, which will be covered in Chemistry 345.

CIRCLE ONE

(a) 

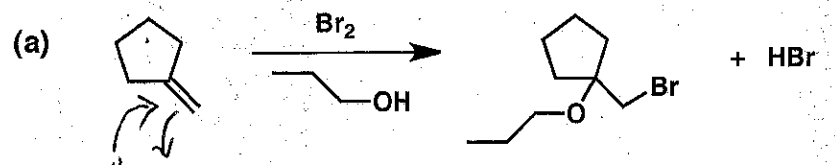
Oxidation
Reduction
(No redox change) +3

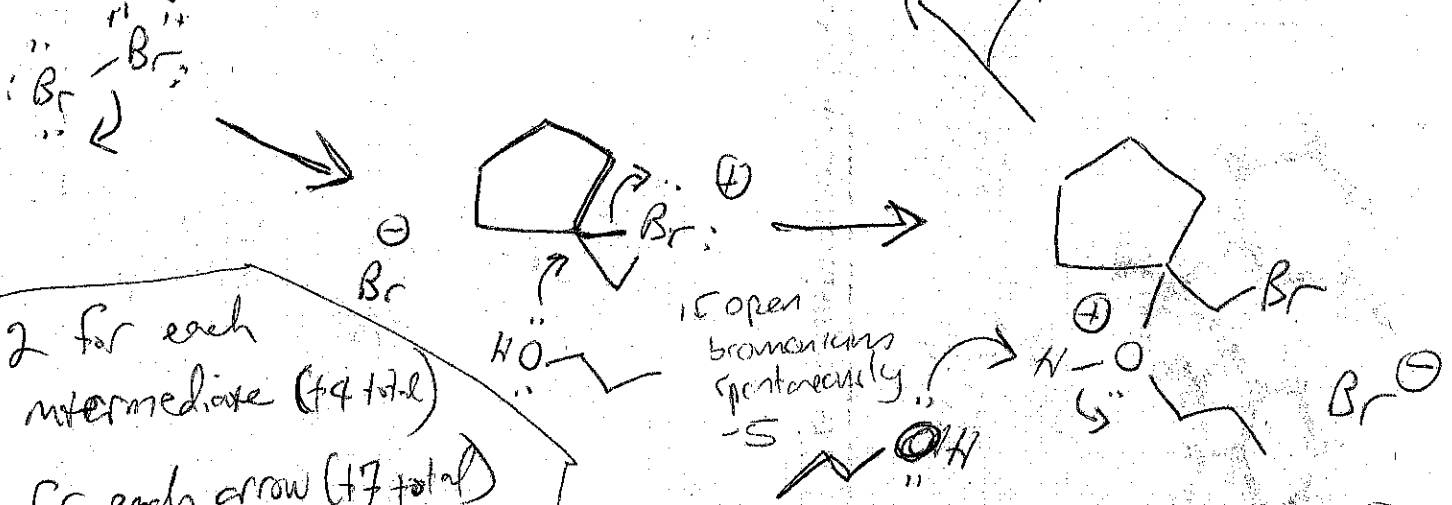
(b) 

(Oxidation) +3
Reduction
No redox change

Name Key (AM)

10. (20 points) Provide a mechanism (curved arrows) for each reaction shown below. Be sure to show intermediates.

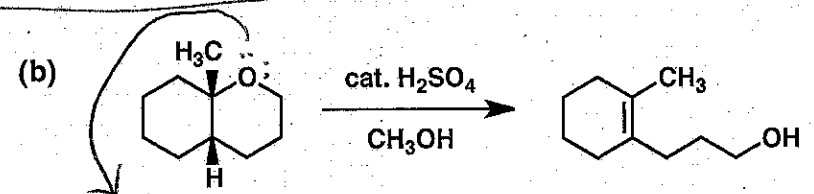


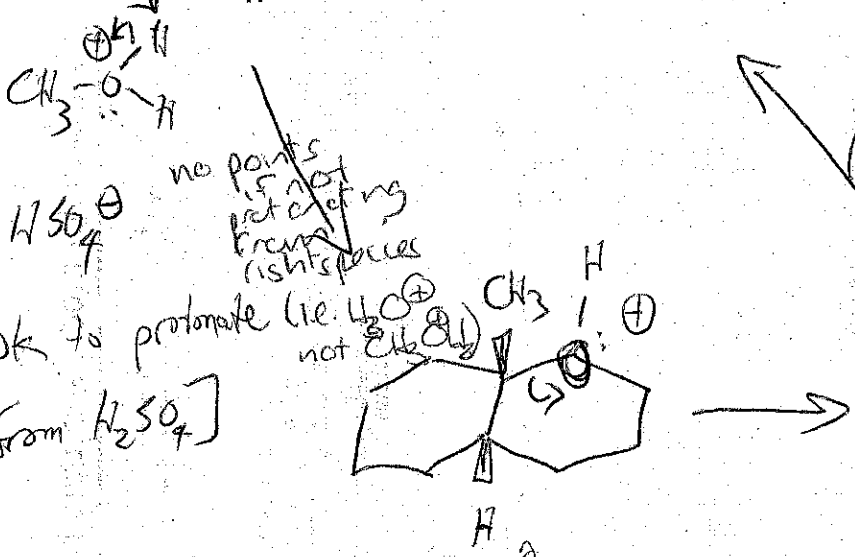


+2 for each intermediate (+4 total)

+1 for each arrow (+7 total)

[Ok if $Br^\ominus$ removes proton, to form HBr]





+2 for each intermediate (+4 total)

+1 for each arrow (+5 total)

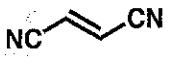
for arrows +1 if all 3 arrows simultaneous (E1) (but no points for 2nd intermediate)

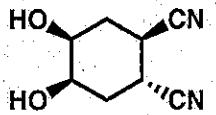
[Ok if internal OH is base, or if $HSO_4^\ominus$ is base]

Name Key (AM)

11. (30 points) Devise a synthetic route from the indicated starting material to the indicated target in each of the two cases below. Each route should be as short and as selective as possible. You may use any other organic molecules and any inorganic reagents in your synthetic plans. Show the expected product after each step in each synthetic route. (Do not provide mechanistic information.)

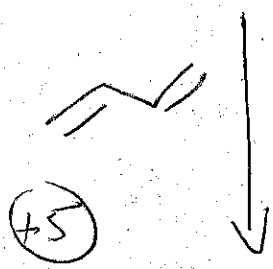
(a)

Starting material = 

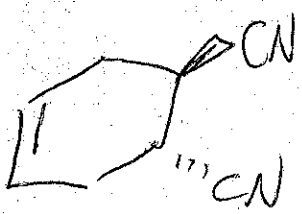
Target = 

(±)

(Diels-Alder)



+5



(±)

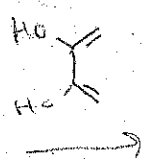
Cat. OsO_4, +3

NMMO, +2

+5

H_2O / acetone

+2 +2 +1



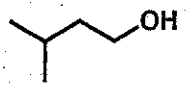
H_2, Pd/c

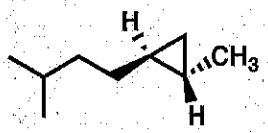
+2 total

-- cont. on next page --

Name Key (AM)

11. (cont.)

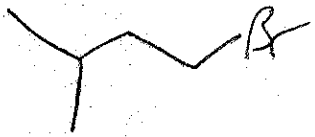
Starting material = 

Target =  (±)

PBr_3 (+5) 2/5 for using HBr

[$SOCl_2$ or P_3Cl, pyr ok]

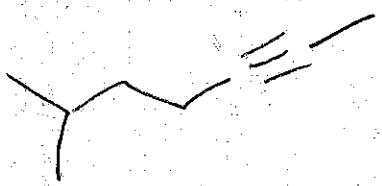
+3/5 for elimination/radical bromination (rare)



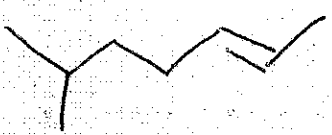
(+5)

$CH_3C{\equiv}C^{\ominus}\ Li^{\oplus}$

4/5 for no counterion



Na^0, $NH_3(l)$ (+5)



(+5) CH_2I_2, Zn-Cu

+3/5 for right reagent, slight mistake in product

2/5 for reagent mistakes