Final Exam
Chemistry 343
Professor Gellman
18 December 2010

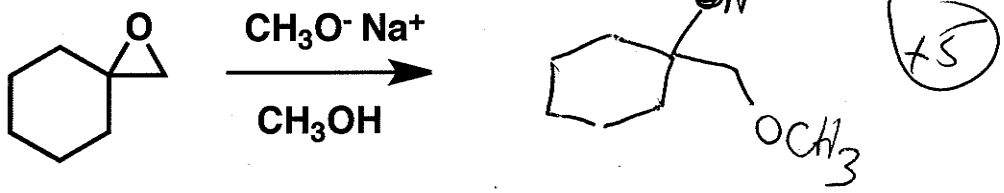
Last Name Answer

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

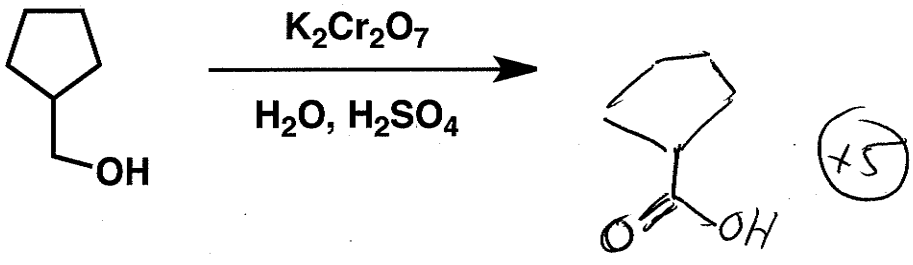
(b)

+5

(c)

+4 for one; +6 for both

(d)



+5

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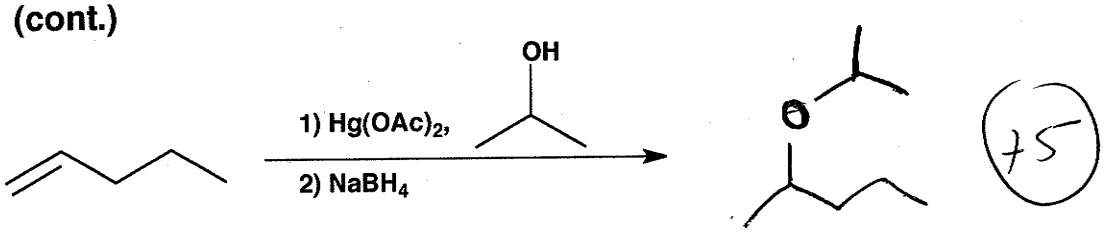
Name _____

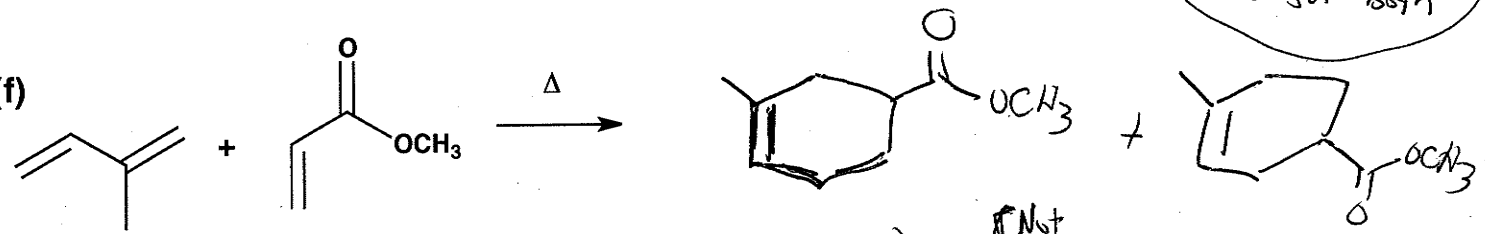
1. (cont.)

(e)



+5

(f)

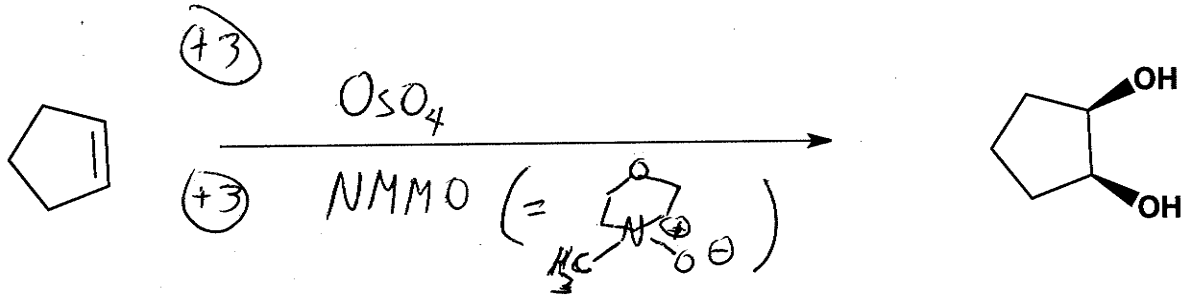


+4 for one; +6 for both

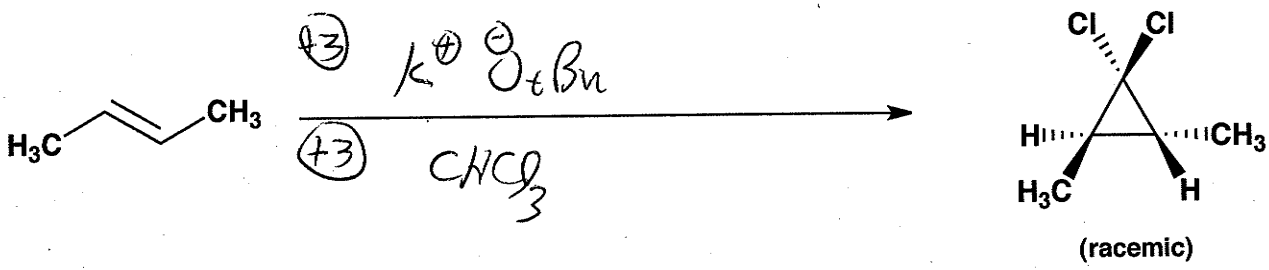
(racemic) <-- [Nu+ required] --> (racemic)

2. (41 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)

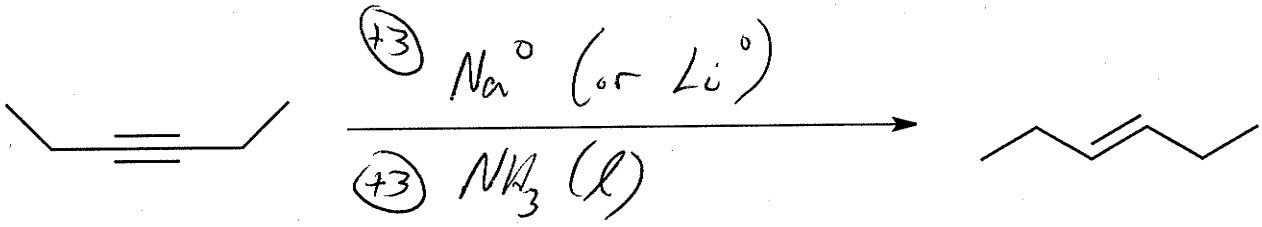


(b)



(racemic)

(c)



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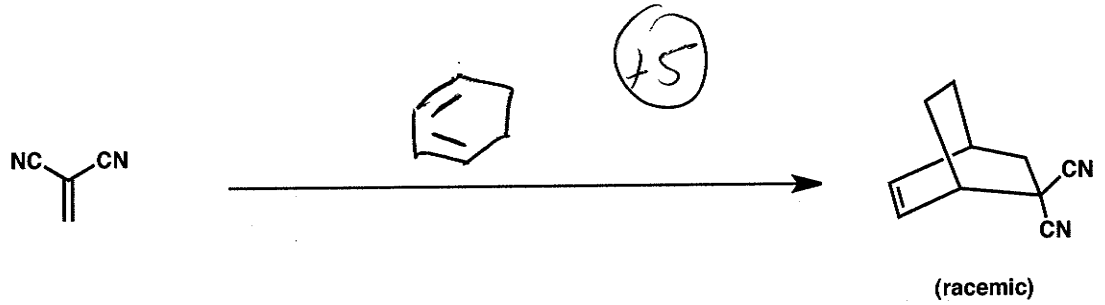
Name _____

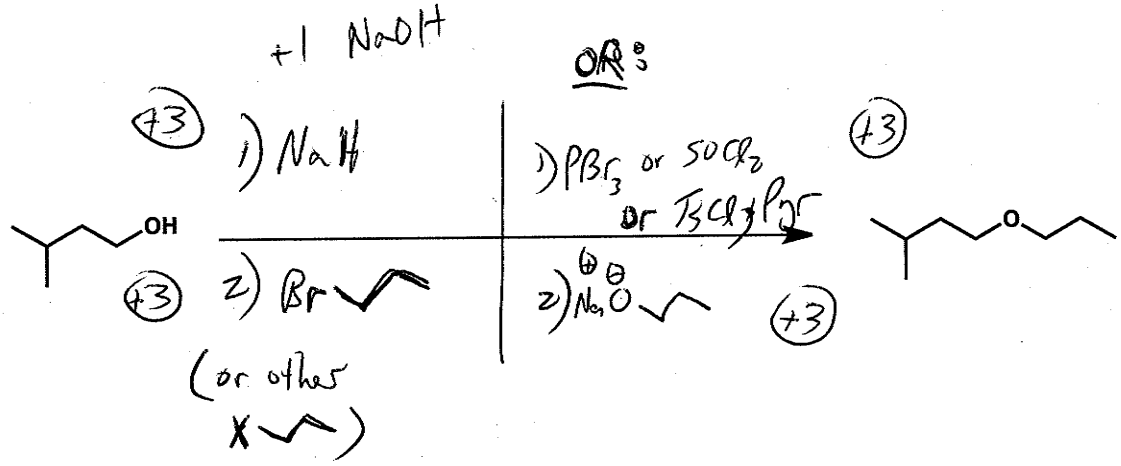
2. (cont.)

(d)

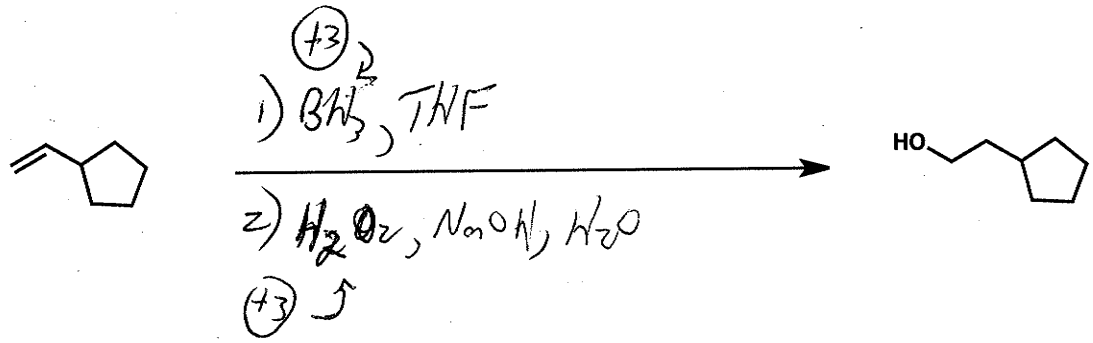


(racemic)

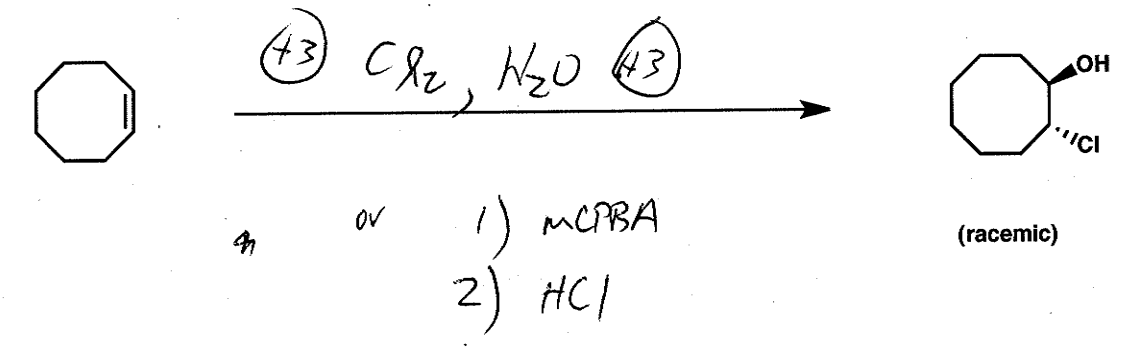
(e)



(f)



(g)

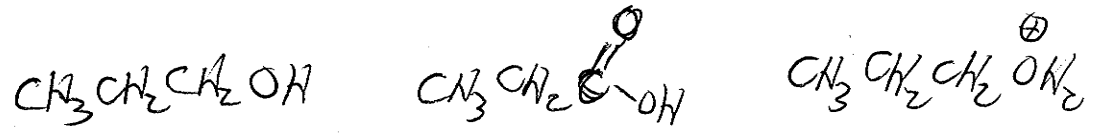


(racemic)

Name _____

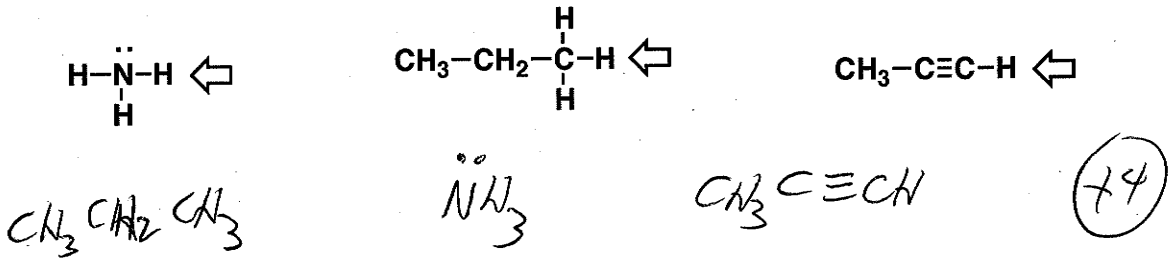
3. (8 points) For each set of three compounds listed below, *redraw them in the order that indicates the highest pK_a on the left and the lowest pK_a on the right.* (The arrow indicates the proton to be considered in each case.)

(a) $CH_3CH_2CH_2-\overset{H}{\underset{|}{\overset{|}{O}}}-H^{\oplus}$ ⇦ $CH_3CH_2CH_2-O-H$ ⇦ $CH_3CH_2-\overset{O}{\overset{\|}{C}}-O-H$ ⇦



+4

(b) $H-\overset{\cdot\cdot}{\underset{H}{N}}-H$ ⇦ $CH_3-CH_2-\overset{H}{\underset{H}{C}}-H$ ⇦ $CH_3-C\equiv C-H$ ⇦

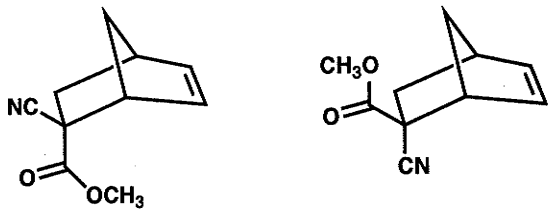


+4

4. (20 points) For each pair of structures below, indicate (on the line below the pair) the relationship between the molecules (at room temperature), choosing from the following possibilities.

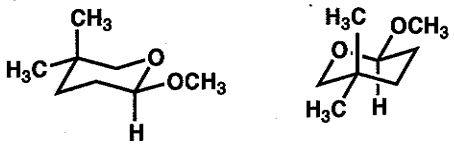
Identical
Enantiomers
Diastereomers
Constitutional Isomers
Non-isomeric

Enantiomers



Diastereomers

+5 each



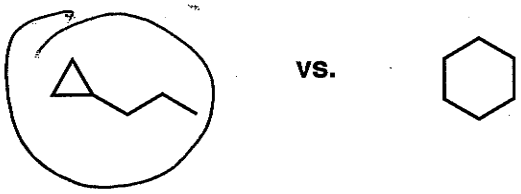
Identical

Identical

Name _____

5. (21 points) The "heat of combustion" (ΔH_c) for a hydrocarbon is the heat associated with complete reaction of the hydrocarbon with O_2, so that every carbon ends up in CO_2 and every hydrogen in H_2O. These reactions are always favorable, which is to say that heat is always released (i.e., $\Delta H_c < 0$).

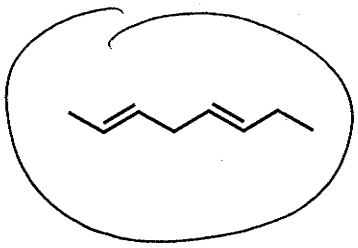
For each of the three pairs of isomeric hydrocarbons below, CIRCLE the one you expect to release MORE heat upon combustion ((i.e., more negative ΔH_c). BRIEFLY explain your choice.

(a)  **vs.**

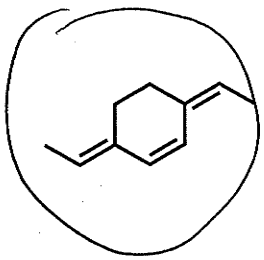
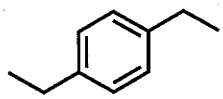
Cyclopropane ring has considerable internal strain, but cyclohexane ring has no internal strain.

+1 for correct circle

+6 for correct explanation

(b)  **vs.** 

The indicated diene is not conjugated. In contrast the other is conjugated and conjugation provides stabilization (which means that less heat is released).

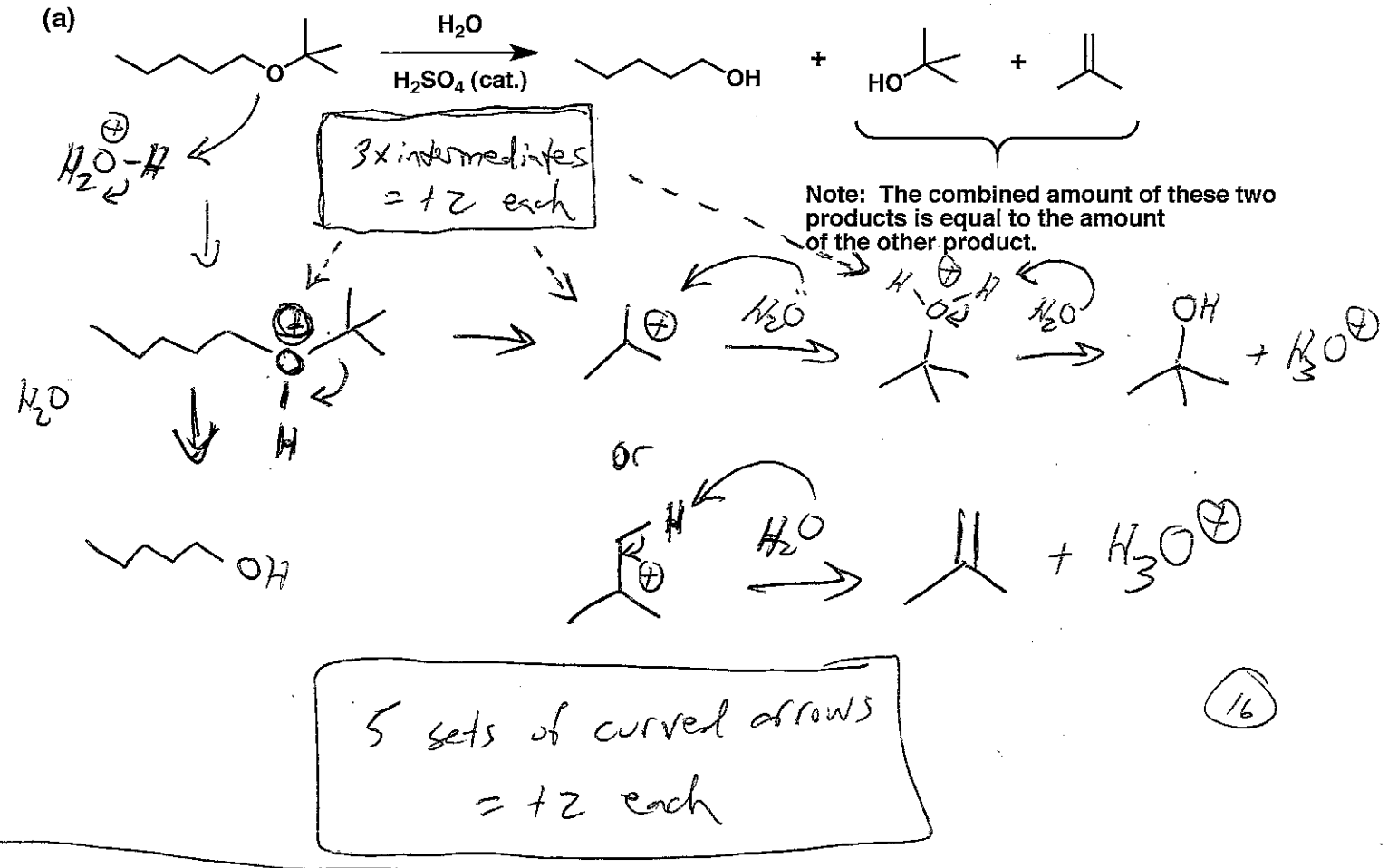
(c)  **vs.** 

The indicated molecule is not aromatic, while the other is aromatic. Aromaticity provides stabilization (which means less energy to be released).

Name _____

6. (30 points) Provide a mechanism (curved arrows) for the reaction shown below. Be sure to show intermediates and all important resonance structures.

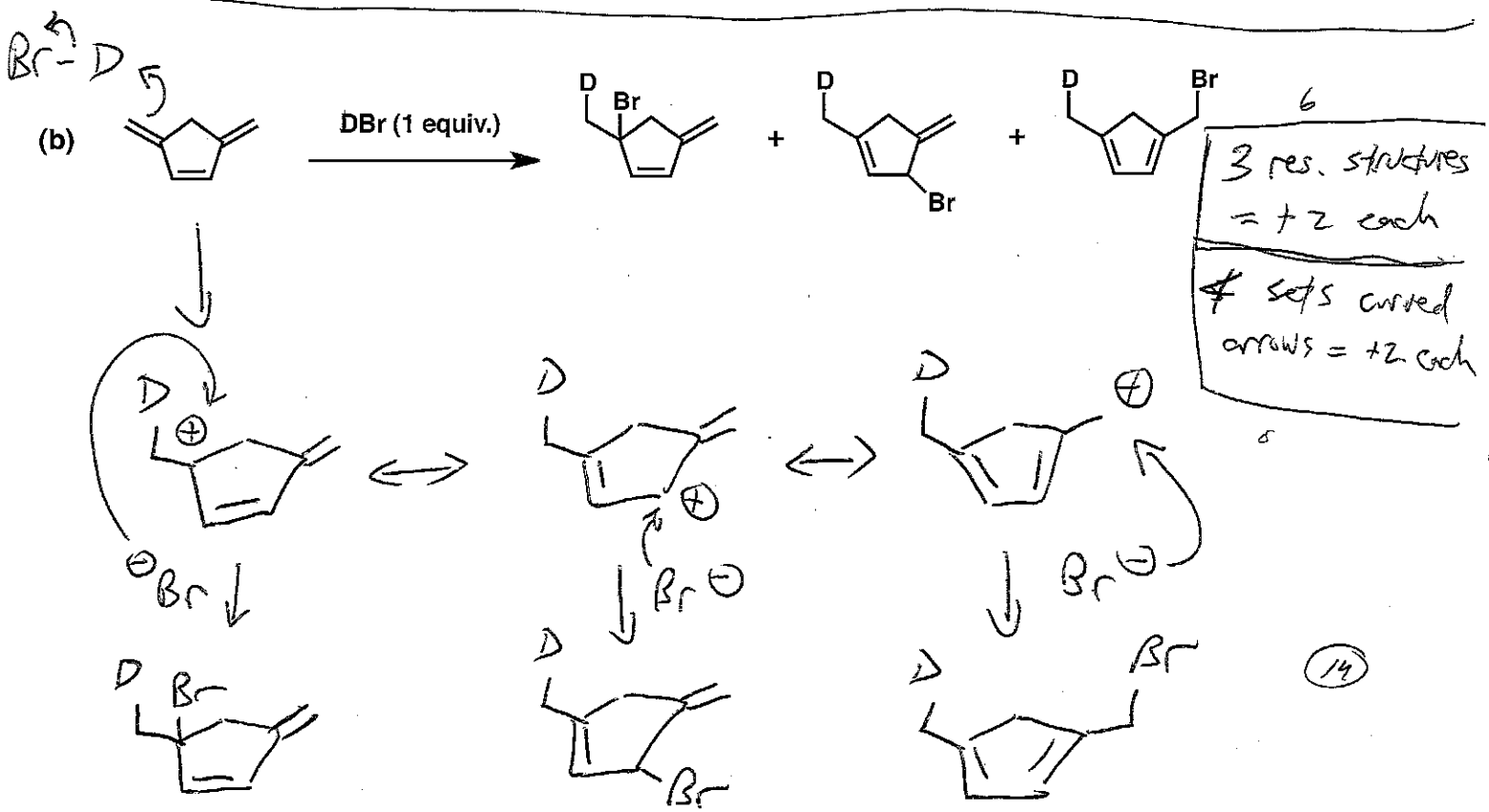
(a)



5 sets of curved arrows = +2 each

16

(b)

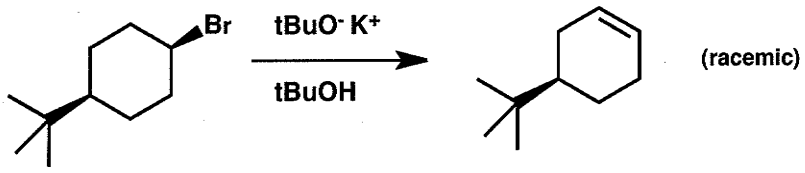


14

Name _____

7. (18 points)

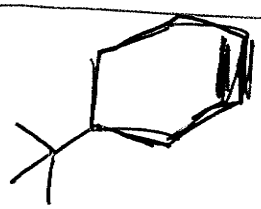
(a) Show the mechanism of the reaction shown below (curved arrows), using a conformationally informative drawing for the starting material.



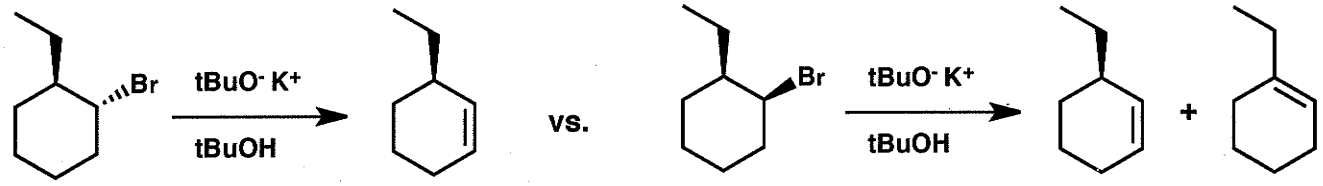
(racemic)

+3 for Chair
+3 for E2 arrows
+2 for "anti" relationship

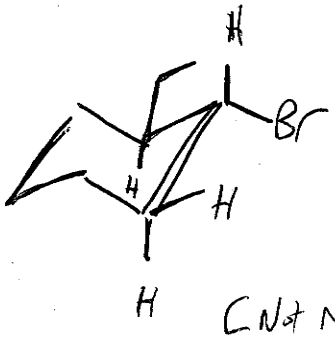
E2 ⇒ Require H anti to leaving group.



(b) Provide conformationally informative drawings for the two stereoisomeric bromides shown below, and use these drawings to explain why the one on the left gives only one product while the one on the right gives two products.



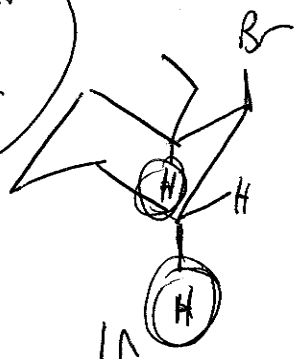
(racemic) (racemic) (racemic) (racemic)



No anti H when Br is equatorial.

[Not required]

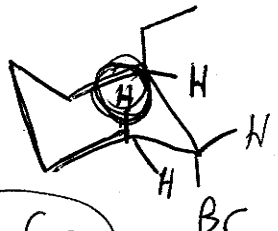
+2 for this chair



+3

Two different anti H's when Br is axial.

∴ Two alkene products

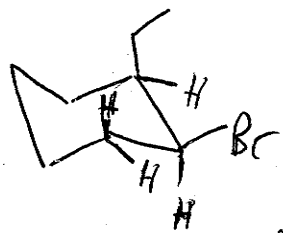


+3

Only one anti H when Br is axial.

∴ Only one alkene.

+2 for this chair



No anti H when Br is equatorial.

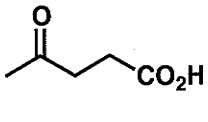
[Not required]

Name _____

8. (10 points) Compound X has the molecular formula $C_{10}H_{16}$.

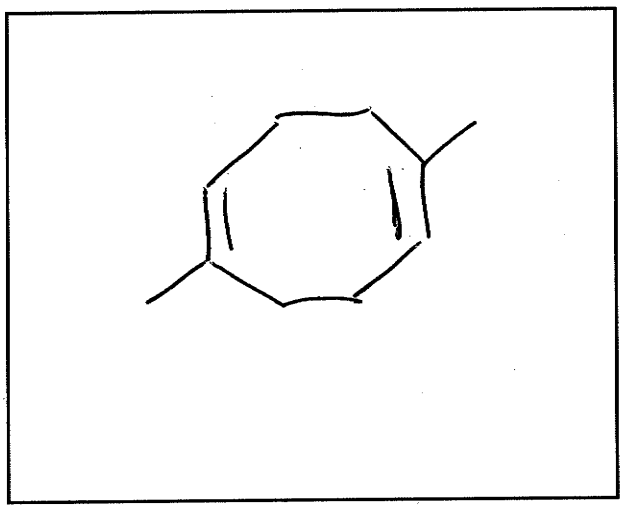
What is the degree of unsaturation (U) of compound X? 3 +3

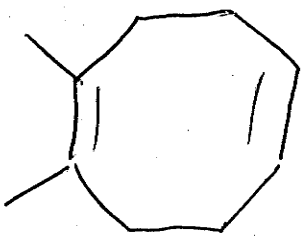
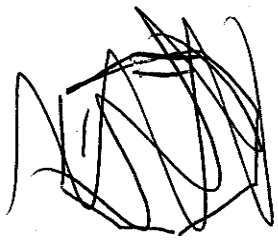
Under the two sets of reaction conditions summarized below, the indicated results are obtained. Based on these results, deduce the molecular structure of compound X.

Compound X $\xrightarrow[2)\ H_2O_2]{1)\ O_3}$ 

Compound X $\xrightarrow[Pd/C]{H_2}$ Two stereoisomeric products with formula $C_{10}H_{20}$.

(Neither product is chiral.)

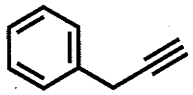
Compound X =  +7

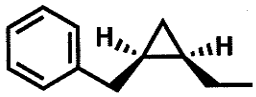
 +3 

Name _____

9. (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.

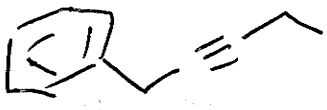
(a)

Starting material = 

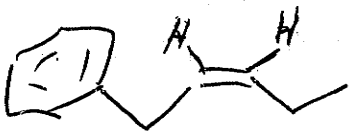
Target = 

(racemic)

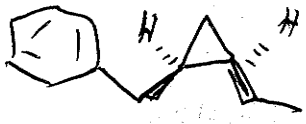
(+5) ↓ 1) $NaNH_2$ 2) 



(+5) ↓ N_2, Poisoned Catalyst



(+5) ↓ CH_2I_2 Zn-Cu



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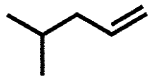
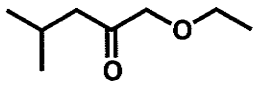
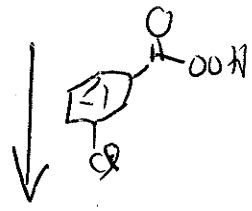
Name _____

9. (cont.)

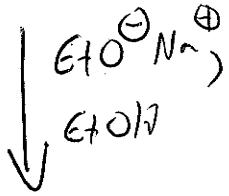
Starting material = 

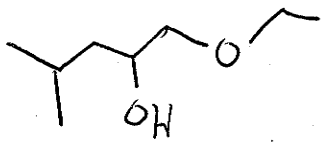
Target = 

+3



+3





+5