



221 W08

(Rogers)

COURSE	NUMBER	SECTION
ORGANIC CHEMISTRY I	CHEM 221	/4 52
EXAMINATION	DATE	TIME
Final Examination	April 17, 2008	1900-2200
INSTRUCTOR		
Dr. C. Rogers		
MATERIALS ALLOWED	NOT ALLOWED	
Calculator, model kit	Notes, cell phones, pagers, electronic dictionaries...	

## Chem 221 --- INTRODUCTORY ORGANIC CHEMISTRY I

LAST NAME: \_\_\_\_\_ FIRST NAME: \_\_\_\_\_

STUDENT NUMBER: \_\_\_\_\_ SIGNATURE: \_\_\_\_\_

### **Instructions: PLEASE READ THIS PAGE WHILE WAITING TO START!**

- Make sure your exam has 12 pages, including this cover page & a periodic table/pK<sub>a</sub> data.
- Write your student ID number on all pages.
- Write all answers legibly in the space provided (use the backs of pages for rough work).
- For full marks: you must show formulae, units & comments throughout your calculations.
- You may detach the periodic table and "potentially useful information" page.
- Read ALL questions quickly BEFORE starting the exam; do the "easy" questions first.
- Suggestion: spend 15 minutes per page to have 45 minutes left to check your work.

#### Mark breakdown:

Page 2. / 8 <sup>7</sup>  
Page 3. / 12  
Page 4. / 13  
Page 5. / 14  
Page 6. / 12  
Page 7. / 8  
Page 8. / 8  
Page 9. / 15  
Page 10. / 3

TOTAL: / 90 (MAXIMUM MARK = 93)

# 1. (8 marks) Circle the word(s) that correctly completes each of the following statements:

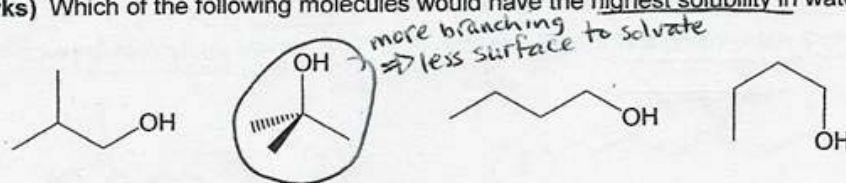
- a) A molecule is most likely to collide with the ( LEAST STABLE / MOST STABLE ) conformation of another molecule if the two compounds are in the same solution.
- b) Simultaneous occupation of a bond's bonding orbital and ( NONBONDING / ANTIBONDING ) orbital leads to bond breakage.
- c) Electrophiles are strongly attracted to the  $\pi$ -electrons in alkenes and alkynes because  $\pi$ -electrons are relatively far from their atoms' nuclei and have high ( ELECTRON DENSITY / POLARIZABILITY ).
- d) According to the Cahn-Ingold-Prelog rules for assigning priorities, higher priority is given to the substituent whose connecting atom has the larger ( ELECTRONEGATIVITY / ATOMIC NUMBER ).
- e) The ( POSITIVE FORMAL CHARGE / OPEN VALENCE ) at the carbocationic center is what causes carbocations to be unstable, reactive intermediates.
- f) Cyclopropane is unusually reactive because of its ( RING STRAIN )  $\pi$ -BONDS ).

not marked. g) Branched versus straight-chain alkanes are examples of ( STEREoisomers / CONFIGURATIONAL / CONSTITUTIONAL ) ISOMERS ).  
*oops - NEITHER*  
*if identify this as wrong, get +1 bonus!*  
*oops!*

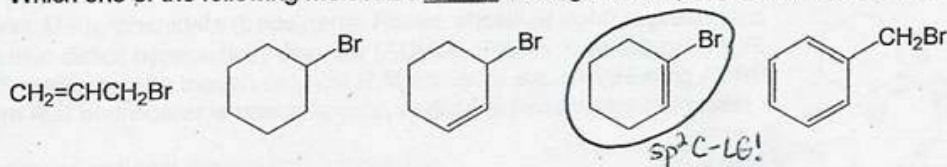
- h) If some strong acid is added to a solution in an alcohol solvent, this will cause some of the alcohol molecules to exist in their ( DEPROTONATED / PROTONATED ) form.

7

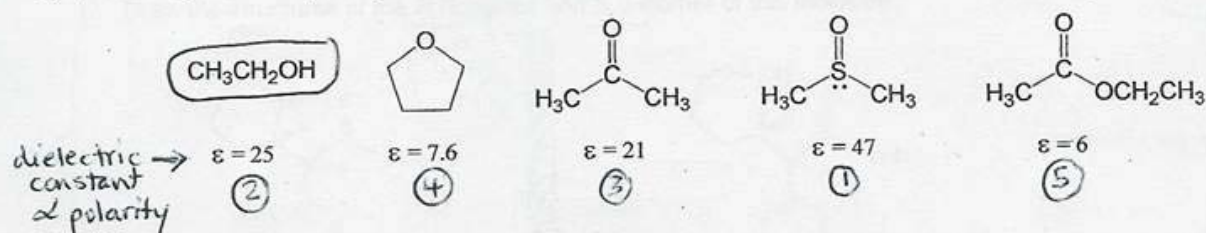
# 2.a) (2 marks) Which of the following molecules would have the highest solubility in water?



b) (2 marks) Which one of the following molecules cannot undergo nucleophilic substitution reactions?



c) (2 marks) Rank the polarity of the solvents shown below, from highest (①) to lowest (⑤):

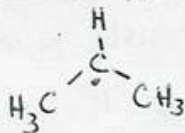


d) (2 marks) Circle any of the solvents in part (c) that would be described as "protic". → means acidic.  
 or, more precisely, means Hydrogen-bond DONOR (H attached to O, N)

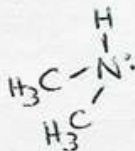
only CH<sub>3</sub>CH<sub>2</sub>OH

# 3. (4 marks) Provide an example of each of the following types of species (i.e., draw their structures).

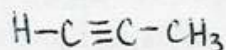
a) a secondary radical



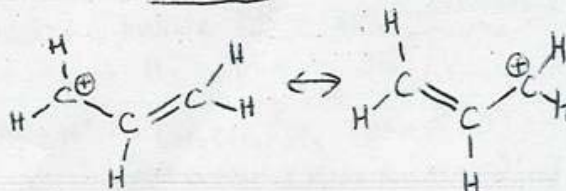
b) a secondary amine: 2 R groups on N



c) a terminal alkyne

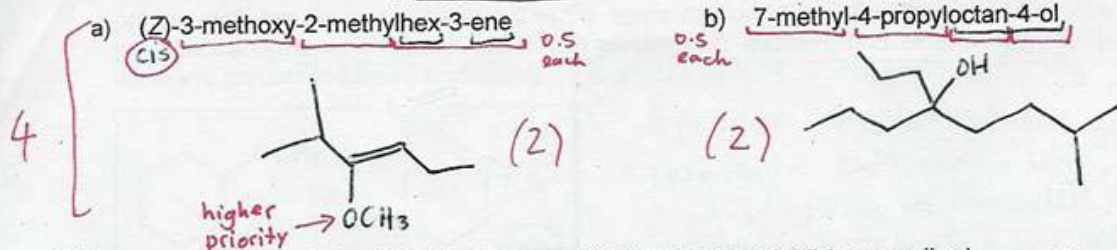


d) a resonance-stabilized carbocation



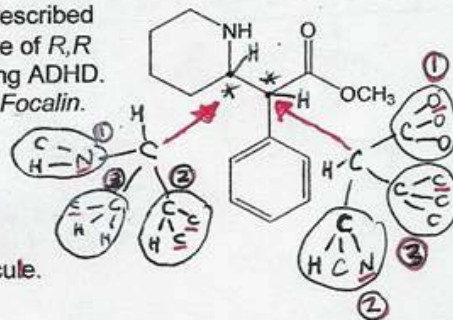


# 4. (4 marks) Draw skeletal (line) structures of the following molecules; include stereochemistry.

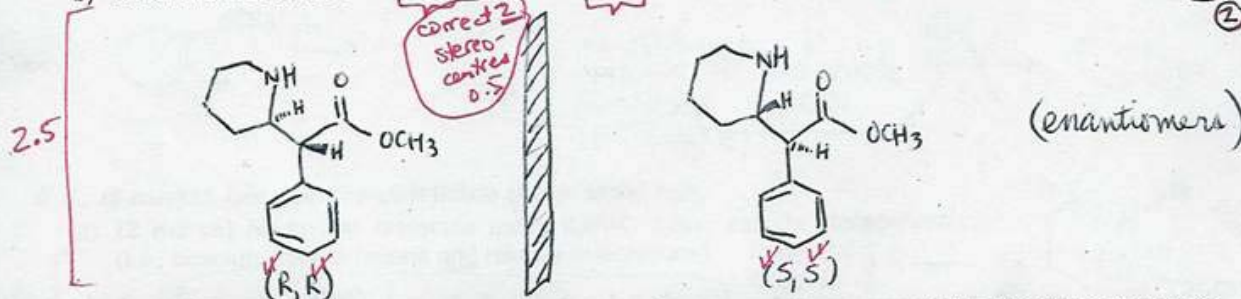


# 5. (5 marks) Methylphenidate (trade name *Ritalin*; shown at right) is prescribed for attention deficit hyperactivity disorder (ADHD). *Ritalin* is a mixture of *R,R* and *S,S* isomers, even though only the *R,R* isomer is active in treating ADHD. The pure *R,R* enantiomer is now also sold, under the trade name of *Focalin*.

- a) Name three functional groups in this molecule.
- 1.5 [ amine, phenyl, carbonyl, alkoxy } → ester



- b) Draw the structures of the *R,R* isomer and *S,S* isomer of this molecule.



- c) Name one property that would differ for these isomers, and one property that would be the same.

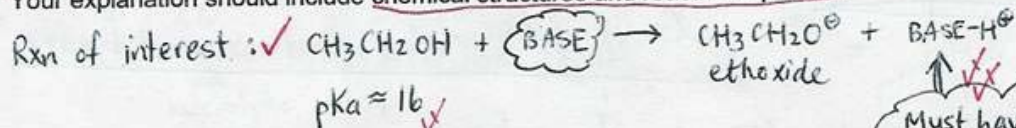
sign of optical rotation } behaviour in a chiral environment

(magnitude same) } m.p., b.p., solubility...  
if only say physical prop.

# 6. (4 marks) Imagine that you wish to prepare a solution of ethoxide anion by adding a base to ethanol.

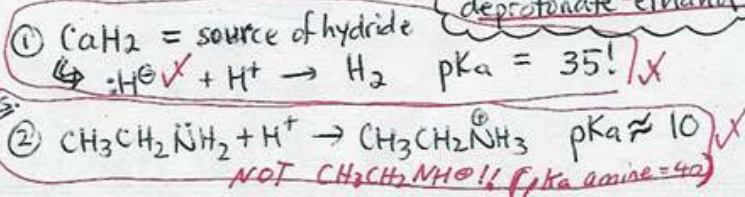
Explain why one of the following bases is suitable while the other will not work:  $\text{CaH}_2$  &  $\text{CH}_3\text{CH}_2\text{NH}_2$

Your explanation should include chemical structures and reaction equations.



Must have  $\text{pKa} > 16$  to be able to use its conjugate base to deprotonate ethanol

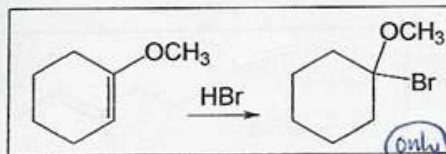
Only hydride is strong enough to deprotonate an alcohol (small, low electronegativity atom with  $\ominus$  charge). An amine is a weak base (high electronegativity atom with zero charge!).



1/3 max.



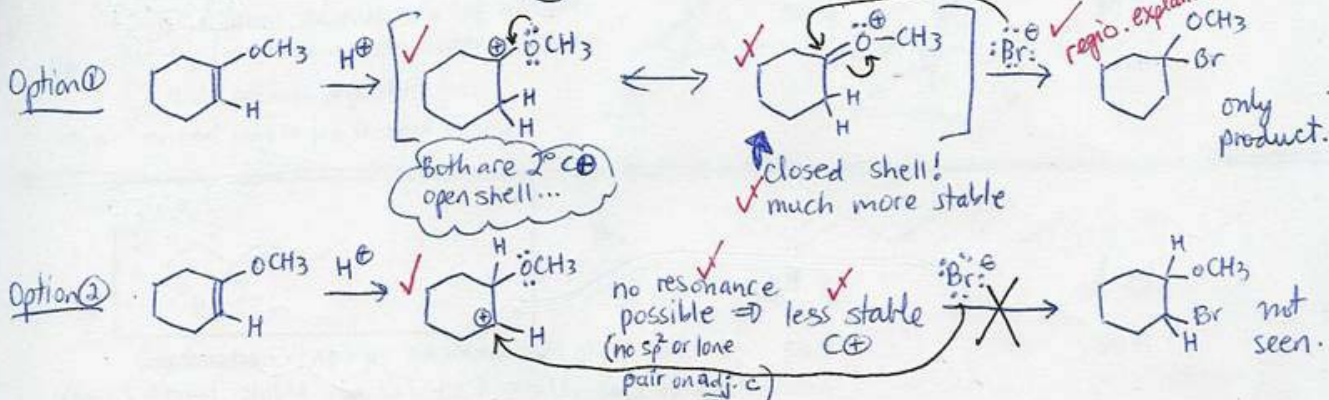
- # 7. (5 marks) For alkenes with a vinylic ether substituent, addition of HBr occurs regioselectively to give a product with the Br and OR bonded to the same carbon atom. For the example below, draw the two possible carbocation intermediates in this electrophilic addition, and explain (using resonance) why the observed product is formed exclusively.



Rephrased Q:

- 2 possible  $C^{\oplus}$  intermediates
- resonance will explain why product forms exclusively.
- resonance:  $\pi$  bonds + lone pair  $e^-$  move...

-1 if give full explanation using level of substitution but no resonance.  
-1.5 if not including rearrangement



- # 8. (9 marks) Consider the alkyl halide shown to the right.

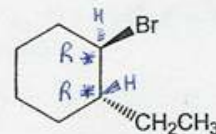
- a) (2 marks) Name the molecule using IUPAC rules; include stereochemistry (i.e., absolute configurations and relative orientations).

2

trans-(R,R)-bromo-2-ethylcyclohexane

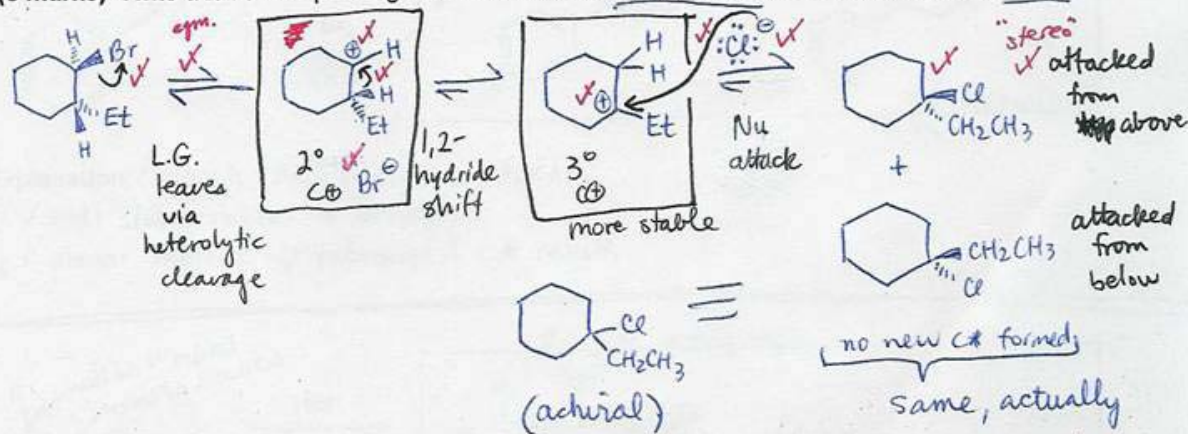
1-bromo } trans  
2-ethyl } cyclohexane

no. 25 each



- b) (5 marks) Write a full arrow-pushing mechanism for the  $S_N1$  reaction of this compound with  $Cl^-$  ion.

5



- c) (2 marks) Is the product from part (b) optically active or not? Explain briefly. (1 if explain all but wrong about being chiral)

2

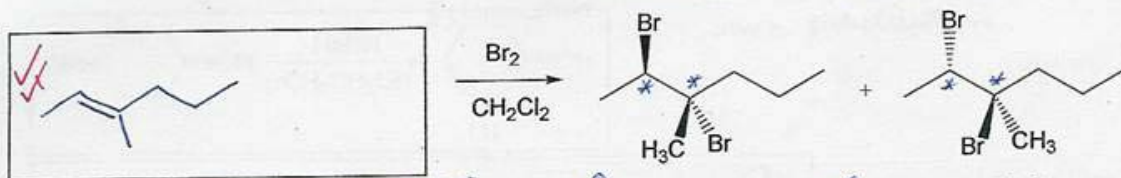
Not optically active, because product is not chiral.

The c attacked by the Nu does not become an asymmetric C, because of the  $C^{\oplus}$  rearrangement. Attack by  $Cl^-$  from either face does occur, but it leads to the same final product.

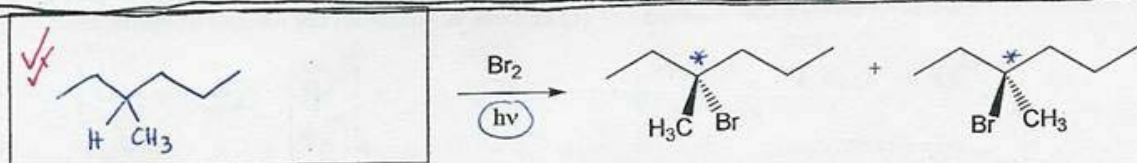
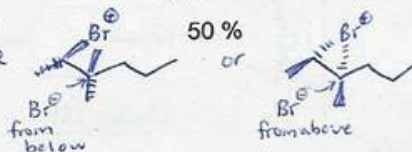
14



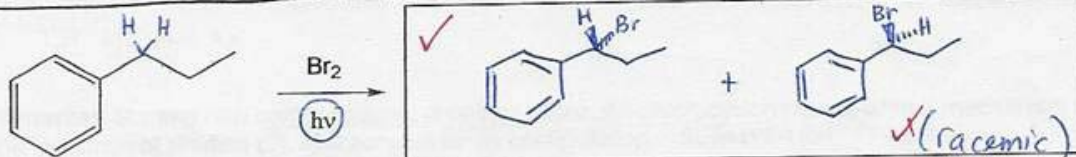
- # 9. (12 marks) There are different ways to attach bromide substituents to different types of carbon chains. For the reactions below: (1) provide the missing reactant or major product(s); include stereochemistry. AND (2) write a few keywords about the mechanism (e.g., type of intermediate...) to explain BOTH the regiochemistry AND the stereochemistry



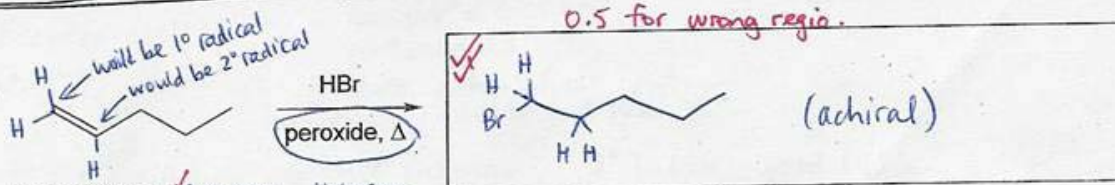
**Explanation:** BROMINATION OF ALKENE  
 stereo: ✓ cyclic bromonium intermediate  
 ✓ anti attack by  $\text{Br}^\ominus$   
 regio: ✓ no real way to see it here, since



**Explanation:** ✓ RADICAL BROMINATION OF ALKANE  
 regio: ✓ most stable radical ( $3^\circ$ ) results from  $\text{H}^\bullet$  abstraction  
 stereo: ✓ racemic because radical intermediate is planar  $\Rightarrow$   $\text{Br}^\bullet$  attaches from either side. equal probability.



**Explanation:** ✓ RADICAL BROMINATION OF ALKANE  
 regio: ✓ most stable radical = benzylic!  
 stereo: ✓ planar radical  $\Rightarrow$  racemized  $\text{C}^*$  results.

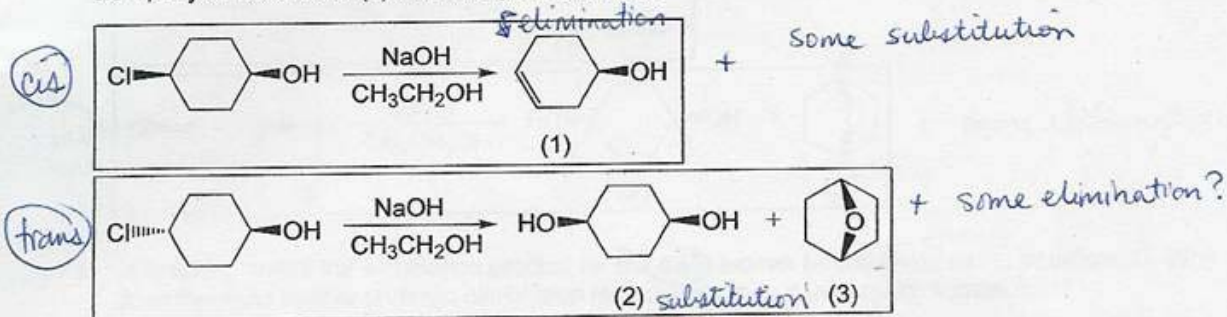


**Explanation:** ✓ RADICAL HYDRO-HALOGENATION OF ALKENE.

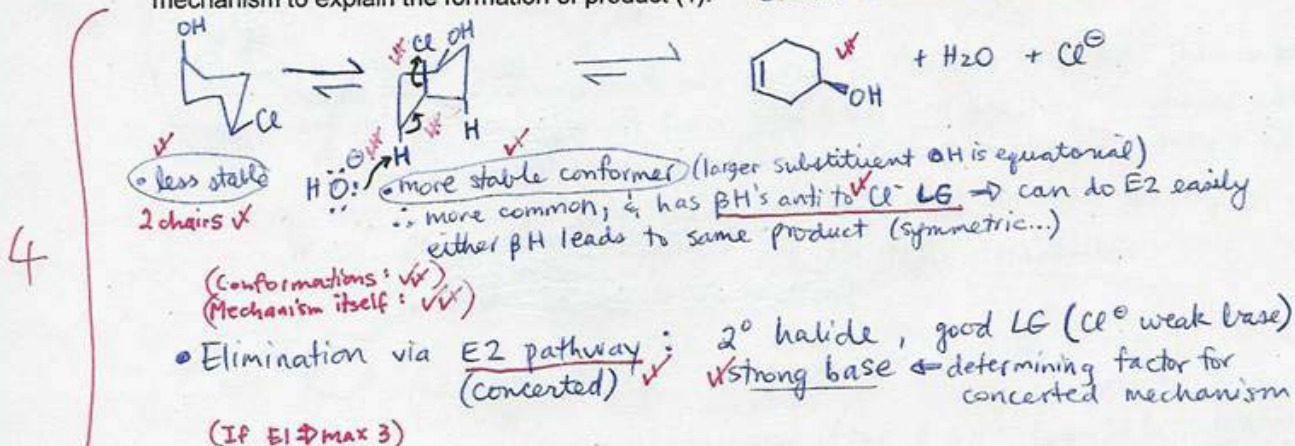
regio: ✓ anti-Markovnikov due to 1st addition of  $\text{Br}^\bullet$  to alkene  $\Rightarrow$  more stable radical is  $2^\circ$ , not  $1^\circ$

12 stereo: ✓ no new stereocentre formed  $\therefore$  planarity of radical has no impact on product.

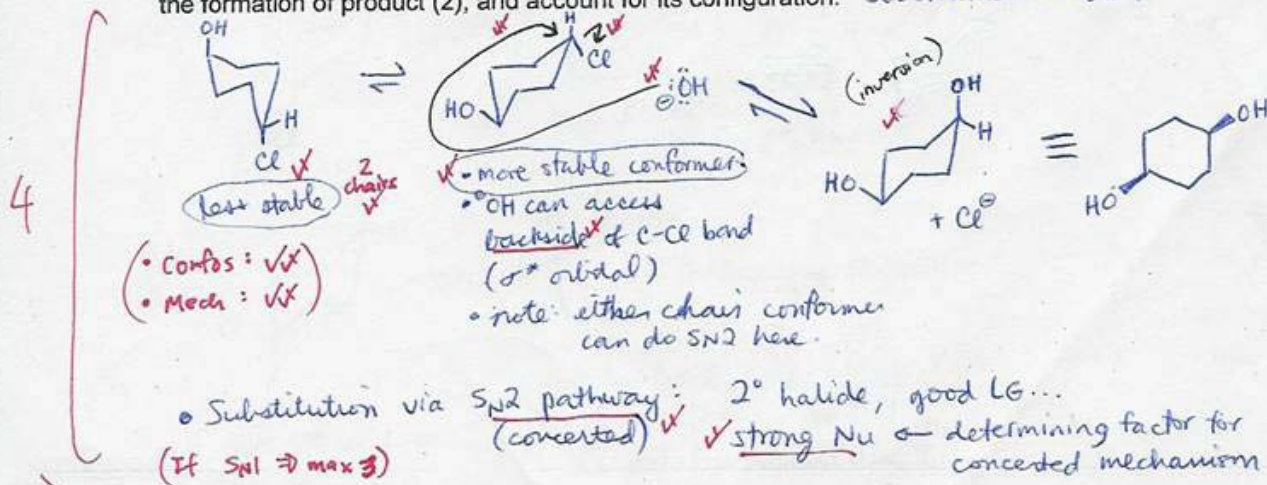
# 10. (8 marks on this page + 8 more on next page...) Under certain conditions, treating *cis*-4-chlorocyclohexanol (top diagram) with NaOH in ethanol results in some substitution but mainly the elimination product (1). Under the same conditions, *trans*-4-chlorocyclohexanol (bottom) yields mainly *cis*-1,4-cyclohexanediol (2) and a bicyclic ether (3).



a) (4 marks) Starting with conformational drawings of *cis*-4-chlorocyclohexanol, write an arrow-pushing mechanism to explain the formation of product (1). Given: ELIMINATION PRODUCT...



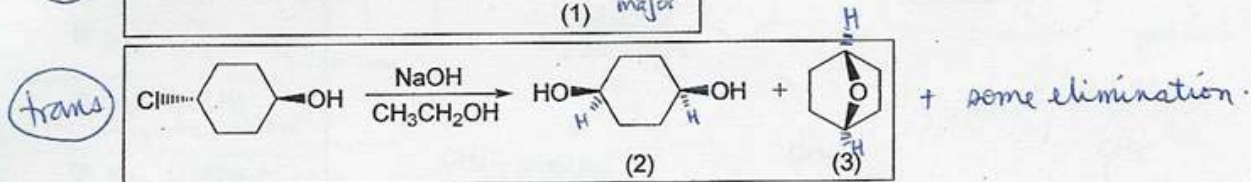
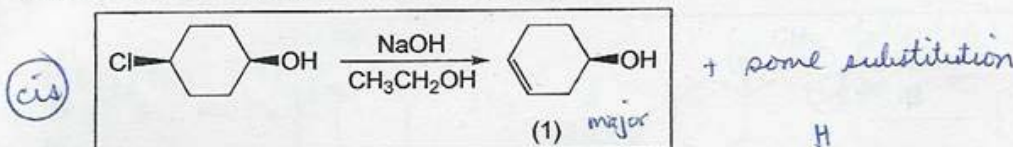
b) (4 marks) Starting with conformational drawings of *trans*-4-chlorocyclohexanol, write a mechanism for the formation of product (2), and account for its configuration. SUBSTITUTION PRODUCT



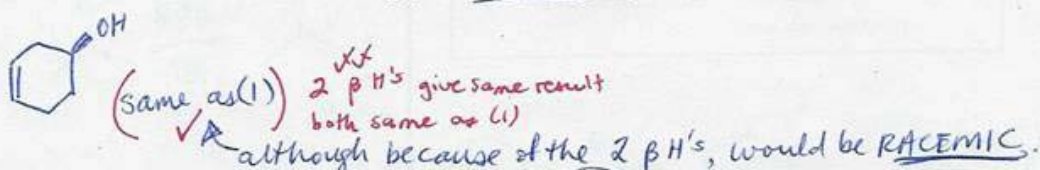
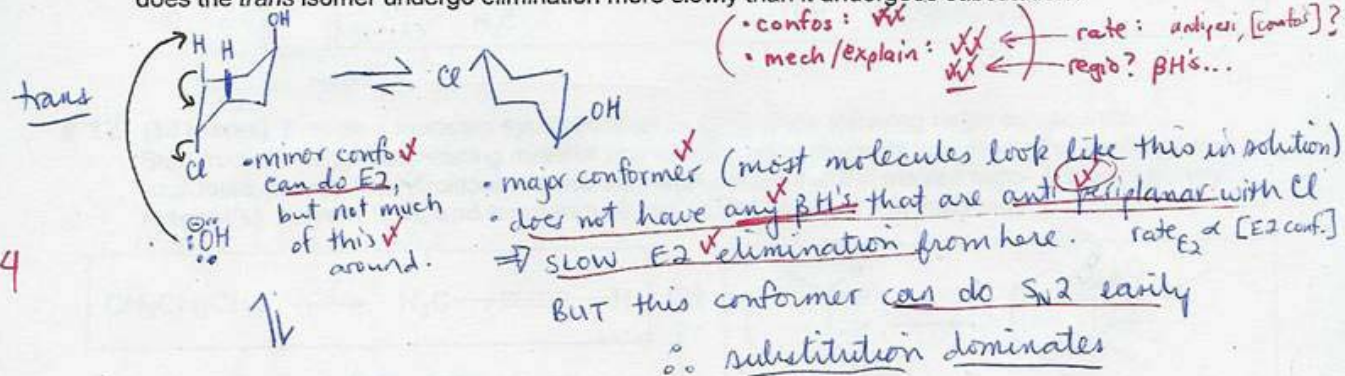
8



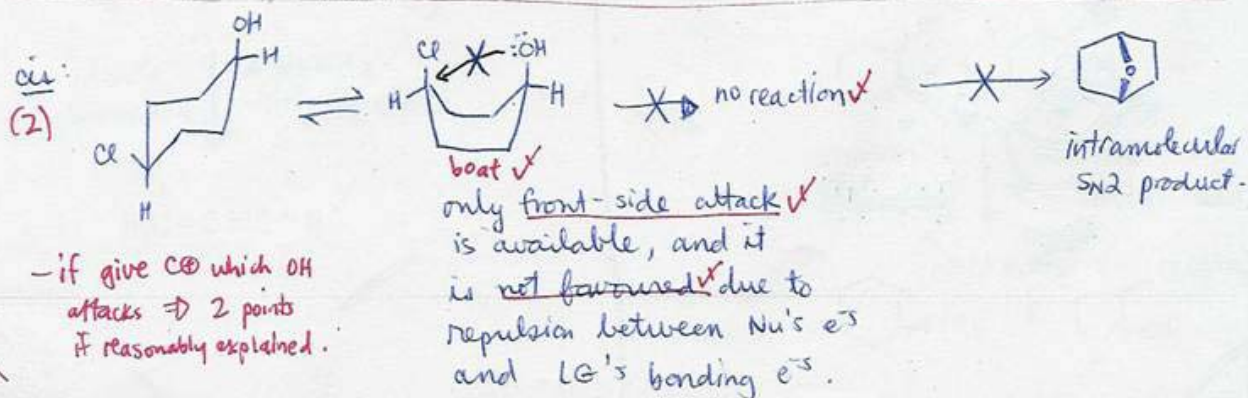
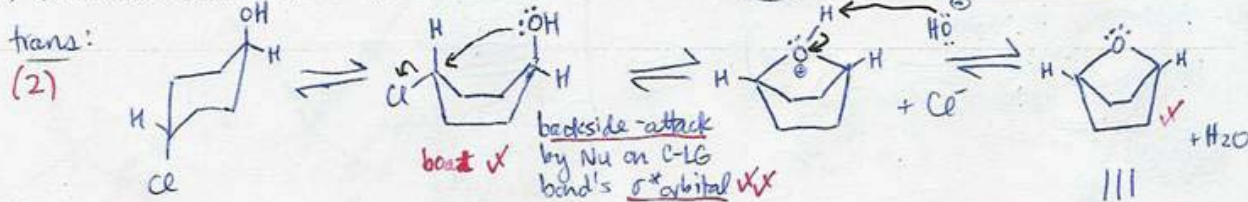
QUESTION # 10 CONTINUED... (8 more marks)



c) (4 marks) Would the elimination product for the **trans** isomer be the same as (1) or different? Why does the **trans** isomer undergo elimination more slowly than it undergoes substitution?



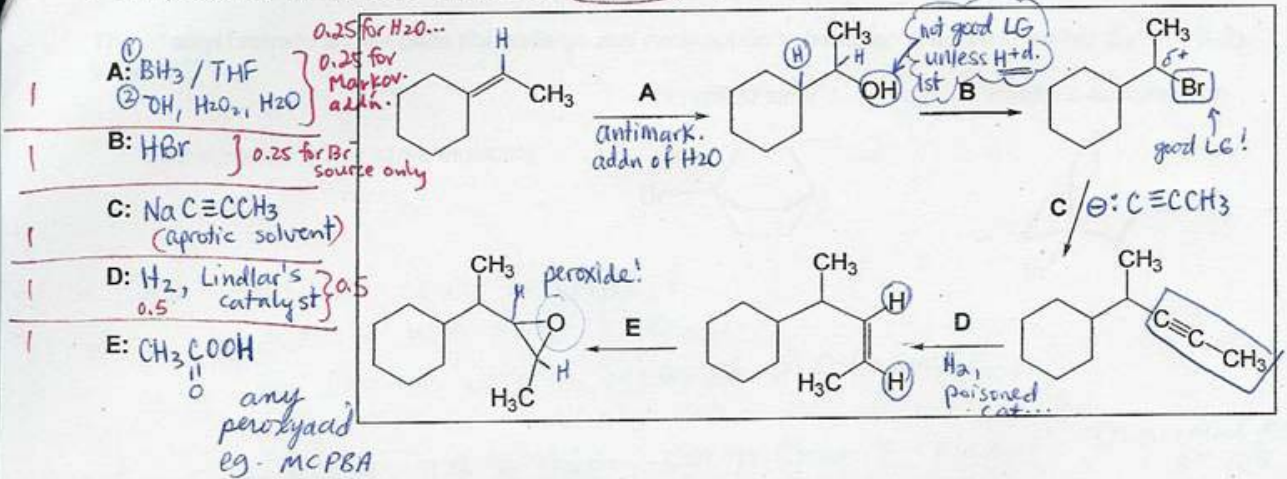
d) (4 marks) Explain why the bicyclic ether (3) is formed from the **trans** isomer but not the **cis** isomer.



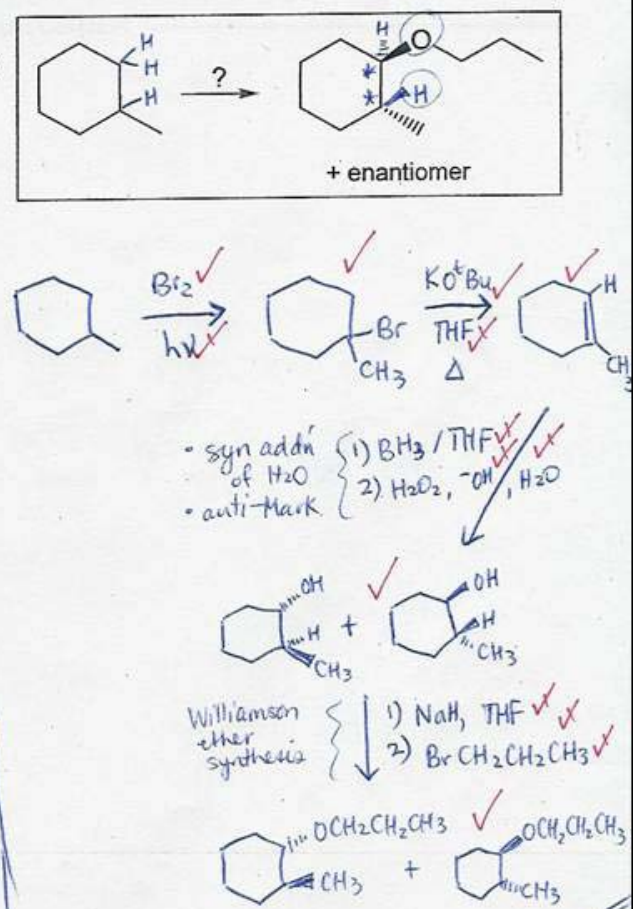
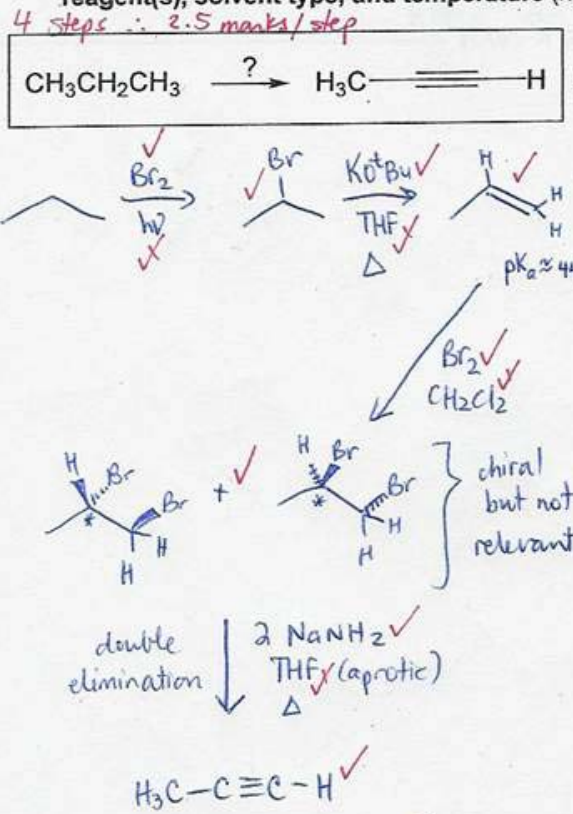
8



# 11. (5 marks) In spaces A – E, write the reagent(s) required to achieve each transformation shown below.



# 12. (10 marks) Provide a multistep synthetic route to ONE of the following target compounds. Start from the suggested starting material and use any other reagents you need. For each reaction in your route, specify the conditions needed for maximum yield of the desired regio- & stereochemistry: reagent(s), solvent type, and temperature (hot vs. cold – only if it is important).



10

15

**BONUS QUESTION: (3 marks)**

The 3° alkyl bromide shown does not undergo any nucleophilic substitution reactions (neither  $S_N1$  nor  $S_N2$ ). Why not?

Two drawings of the same molecule:

Simplified view



Realistic conformation



- $S_N2$ : does not occur for 3° RX ✓  
 due to high steric hindrance ✓  
 Nu cannot access backside of C-Br bond ✓
- $S_N1$ : requires LG to leave,  $C^+$  to form = planar. ✓ ⇒ normal for 3° RX...  
 here: ring strain prevents planarization  
 ie: rings will make it difficult to achieve 120°  
 bond angles ✓

----- HAVE A GOOD SUMMER -----