

Concordia

UNIVERSITY

COURSE ORGANIC CHEMISTRY I

NUMBER CHEM 221

SECTION /2 01

EXAMINATION
FINAL EXAMINATION

DATE DECEMBER 4, 2003

TIME 9:30 am

INSTRUCTOR

DR. CERRIE ROGERS

MATERIALS ALLOWED:

NO

YES (PLEASE SPECIFY)

MOLECULAR MODEL KITS

CALCULATORS ALLOWED:

NO

YES

LAST NAME: _____

FIRST NAME: _____

STUDENT NUMBER: _____

SIGNATURE: _____

Instructions:

- **Make sure your exam has 12 pages including this cover page and the periodic table.**
- **Write your name on all pages.**
- **Write all answers in the space provided.**
- **You must answer ALL of the first 14 questions. The final question is an optional bonus question.**
- **Read questions carefully before answering.**
- **Molecular models and calculators are allowed.**
- **A periodic table and table of pK_a values are provided.**

Mark breakdown:

Page 3. / 17

Page 4. / 9

Page 5. / 15

Page 6. / 10

Page 7. / 12

Page 8. / 15

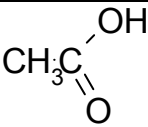
Page 9. / 16

Page 10. / 18

Page 11. / 6 BONUS

TOTAL: / 112 (MAXIMUM MARK = 120)

TABLE OF pKa VALUES

Compound	pK _a
CH ₃ CH ₂ CH ₂ CH ₃	>51
CH ₄	51
NH ₃	38
HCCH	25
(CH ₃) ₃ COH	19
CH ₃ CH ₂ OH	17
CH ₃ OH	15.5
H ₂ O	15.7
HCN	9
	4.7
HF	3.2
HN ₃	3
CH ₃ CH ₂ OH ₂ ⁺	-2.4
H ₂ SO ₄	-5.2
HCl	-7
HI	-9

#1. (14 MARKS) Circle TRUE or FALSE for the following statements.

- a) n-Butanol has a lower boiling point than diethyl ether. TRUE/FALSE
- b) According to IUPAC rules, an alcohol has priority over a halide. TRUE/FALSE
- c) Stereoisomers are molecules that have the same connectivity of atoms, but different 3-dimensional arrangements of these atoms. TRUE/FALSE
- d) If we know the R/S configurations of the stereocentres in a chiral molecule, we can predict the direction in which that molecule will rotate plane-polarized light. TRUE/FALSE
- e) A racemic mixture can be “resolved” into pure enantiomers if we can convert the enantiomers into diastereomers using a chemical reaction that can later be reversed. TRUE/FALSE
- f) An electron donating substituent on the carbon adjacent to the nitrogen atom increases the basicity of an amine. TRUE/FALSE
- g) Markovnikov’s rule is based on the fact that an electrophile will add to a π -bond to yield the more stable carbocation intermediate. TRUE/FALSE
- h) In an elimination reaction, the thermodynamically favoured alkene product is known as the Saytzeff (or Zaitseff) product. TRUE/FALSE
- i) Polar protic solvents stabilize carbocationic intermediates. TRUE/FALSE
- j) Highly polarizable, or “soft”, Lewis bases interact better with protons than with electrophilic carbon atoms. TRUE/FALSE
- k) It is easier to deprotonate an sp^3 hybridized carbon than an sp hybridized carbon. TRUE/FALSE
- l) $AlCl_3$ is a powerful nucleophile. TRUE/FALSE
- m) A Lewis base can act both as a nucleophile and as a Brønsted base. TRUE/FALSE
- n) When treated with sodium iodide in acetone solution, a tertiary alkyl halide will react faster than a primary alkyl halide. TRUE/FALSE

#2. (3 MARKS) Lithium diisopropyl amide $[(CH_3)_2CH]_2N^-$, known as “LDA”, is commonly used as a base in organic transformations. Which of the following reagents could be used to completely deprotonate diisopropyl amine $[(CH_3)_2CH]_2NH$ in order to prepare this anion?

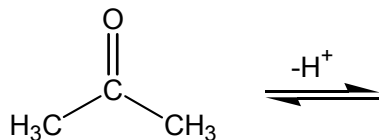
I LiF

II CH_3CH_2OLi

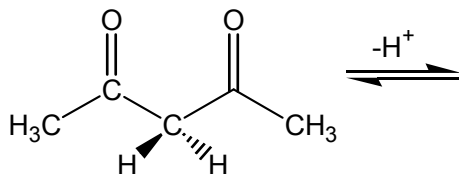
III $CH_3CH_2CH_2CH_2Li$

- a) I, II, and III
- b) I and II only
- c) II and III only
- d) I only
- e) III only

#3. (4 MARKS) 2,4-Pentanedione is considerably more acidic than propanone (acetone). Draw the structure of the conjugate base of each acid, and account for the greater stability of the conjugate base of 2,4-pentanedione.



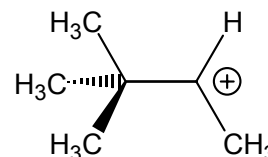
2-Propanone
 $pK_a = 22$



2,4-Pentanedione
 $pK_a = 9$

#4. (5 MARKS) Imagine that the following carbocation has formed:

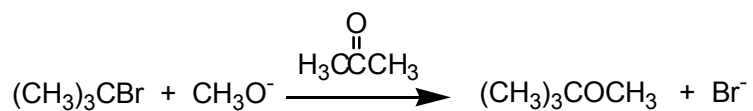
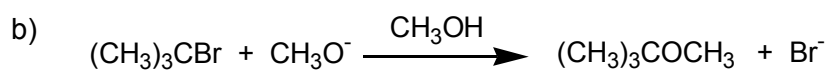
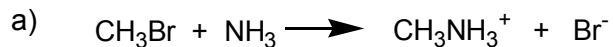
a) Why is this species so reactive?



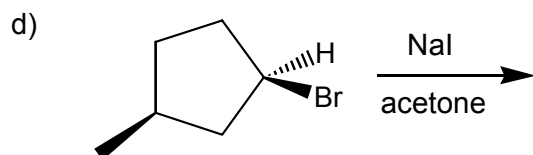
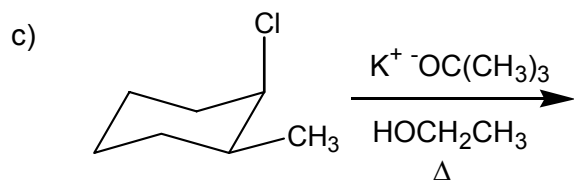
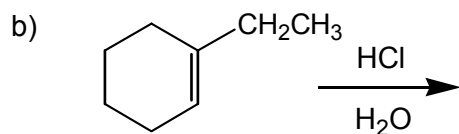
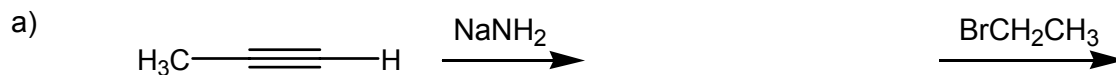
b) What will this species do immediately after forming in order to increase its stability? Illustrate this process with curved arrows representing the movement of electrons, AND explain why this process increases the stability of the carbocation.

c) Name a type of reaction that involves a carbocation intermediate.

#5. (3 MARKS) Which reaction in each of the following pairs will take place more rapidly?

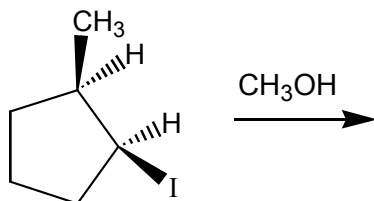


#6. (12 MARKS) The major product(s) of the following reactions would be:

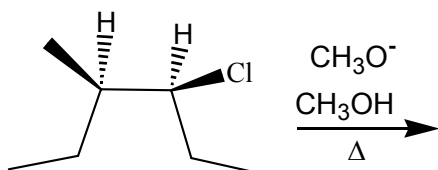


#7. (10 MARKS) Write mechanisms for TWO of the following reactions. Show full, detailed mechanisms that illustrate step-by-step how the reaction occurs: use curved arrows for “electron pushing”, include the transition state and all intermediates (show rearrangements where appropriate), and clearly indicate the stereochemistry of the products.

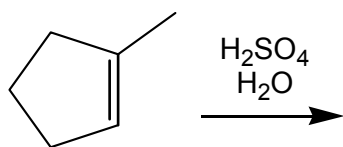
a) An S_N1 substitution:



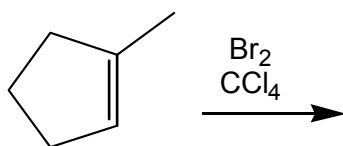
b) An $E2$ elimination:



c) An electrophilic addition: hydration of an alkene:

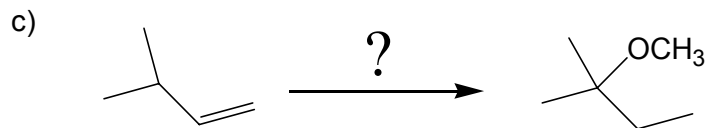
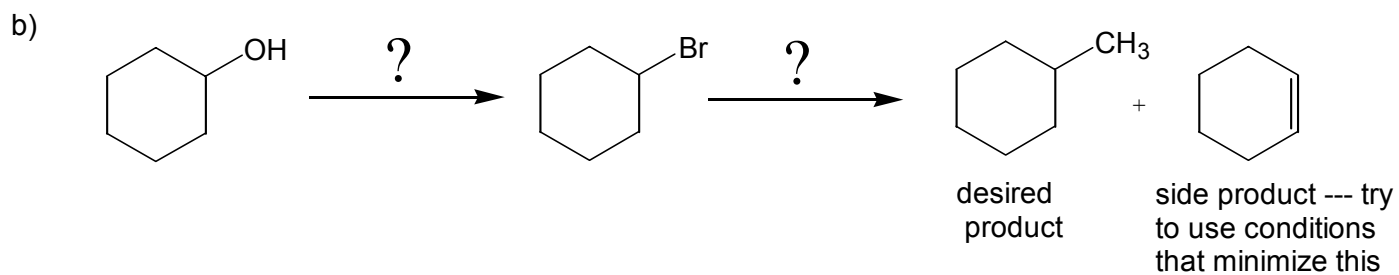
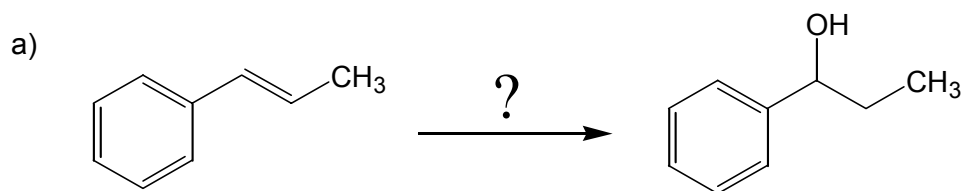


d) An electrophilic addition: bromination of an alkene:



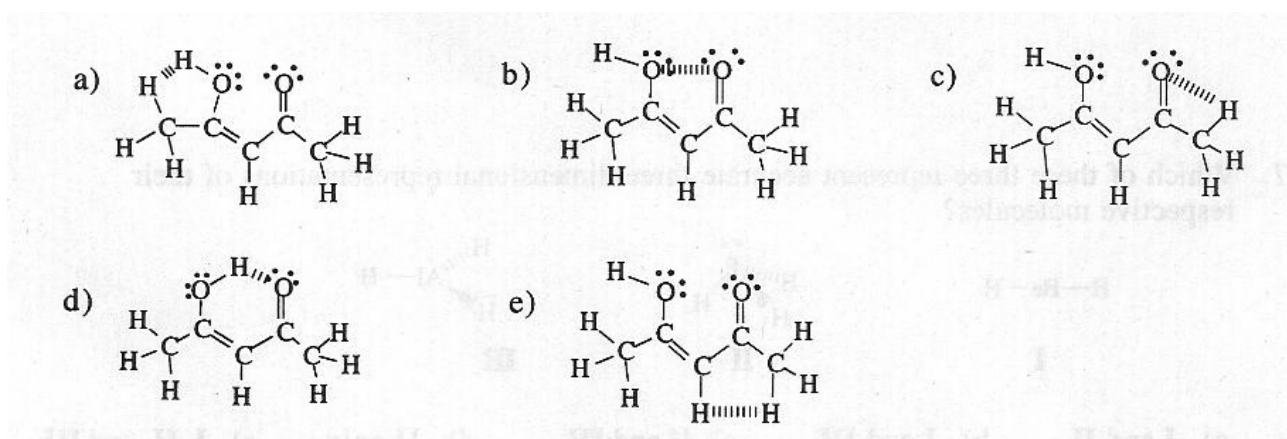
#8. (12 MARKS) Suggest reagents and solvents for each of the following synthetic transformations.

Note that these transformations may require more than one step.



PART B

#9. (3 MARKS) CIRCLE YOUR CHOICE. The “enol” form of acetylacetone is stabilized by an intramolecular hydrogen bond. Which of these structures best represents this enol form?



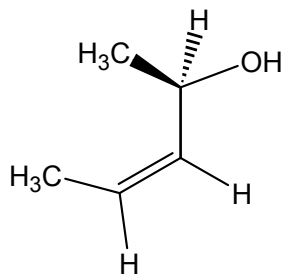
#10. (8 MARKS) Draw 3-dimensional representations of the following compounds, showing the stereochemistry of the stereocenters.

(a) (2*R*,4*R*)-4-hydroxy-2,5-dibromo-2-methylpentanoic acid

(b) (4*E*)-(2*S*,3*R*)-3-methoxy-2-methylhex-4-en-1-ol

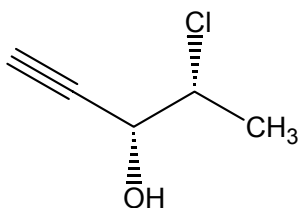
#11. (4 MARKS) CIRCLE ONE. How many optically active stereoisomers does this substance have?

- a) 0
- b) 1
- c) 2
- d) 3
- e) 4

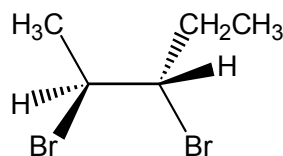


#12. (8 MARKS) Give the IUPAC names for the following compounds, including stereochemistry.

a)



b)



#13. (8 MARKS TOTAL) Consider the compound in #12(b).

a) (2 marks) Draw and name a diastereomer of this compound.

b) (3 marks) Draw a Newman projection that represents the conformation shown in #12(b), looking down the bond between the bromine-substituted carbon atoms.

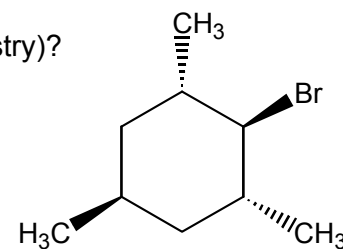
c) (3 marks) Is this the most stable conformation for this molecule? Why or why not? Explain in terms of electrostatic (*i.e.*, gauche vs. eclipsed bonds) and steric interactions.

#14. (18 MARKS TOTAL) The questions on this page deal with the following substituted cyclohexane:

a) (4 marks) What is the IUPAC name of this compound (including stereochemistry)?

b) (1 mark) Is this compound chiral? Circle one: YES / NO

c) (2 marks) If you think it is chiral: draw its enantiomer.
If you think it is achiral: what makes it achiral?



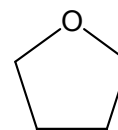
c) (1 mark) Is this compound optically active? Circle one: YES / NO

d) (2 marks) Pick the solvent in which you expect this compound to be most soluble:

(i) ethanol

(ii) hexane

(iii) THF



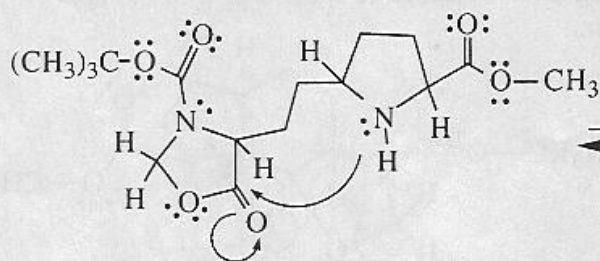
e) (2 marks) Draw the interconversion of the two chair conformations for this substituted cyclohexane.

f) (2 marks) Circle the preferred conformation from part (e). Why is that conformation more stable?

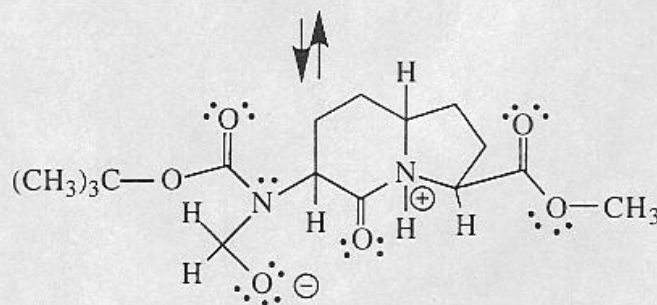
g) (5 marks) This compound can undergo an E2 elimination if it is heated in a solution containing KOH. Which conformation is the one that participates in this reaction? Why? You may wish to support your argument with Newman projections and a discussion of the orbitals involved in the reaction.

OPTIONAL BONUS QUESTION (8 marks)

Chemists in the pharmaceutical (drug/medicine) industry have targeted molecules that mimic the action of amino acids as being important to prepare. The preparation of one such compound was reported recently (*Tetrahedron Lett.* **1997**, 37, 6483). Following the implications for bonding changes of the curved-arrow convention, draw the single intermediate structure that follows from the starting compound, and then add the set of arrows to the structure you have drawn that would explain the formation of the next intermediate, as shown.



Draw: the structure implied by the curved arrows AND the curved arrows needed to transform it to the next structure.



B1: Draw the structure and 'arrow pushing' steps as indicated in the box.

B2: How many chiral carbons are there in the final product?

B3: Circle the functional groups in the final product that would be protonated in acidic solution.

----- * HAPPY HOLIDAYS! * -----