

ORGANIC CHEMISTRY I

CHEM 221

/4 02

Final Examination

April 20, 2005

0900-1200

Dr. Carrie ROGERS

x

periodic table & pK_a data table provided

non-programmable calculators allowed

x

molecular model kits allowed

Chem 221 --- ORGANIC CHEMISTRY I

LAST NAME: _____ FIRST NAME: _____

STUDENT NUMBER: _____ SIGNATURE: _____

Instructions: PLEASE READ THIS PAGE WHILE WAITING TO START!

- ***Make sure your exam has 13 pages, including this cover page.***
- ***You may detach the two pages containing the periodic table and pK_a data if you wish.***
- ***Write your student ID number on all pages.***
- ***Write all answers legibly in the space provided (use the backs of pages for rough work).***
- ***Non-programmable calculators are allowed; cell phones & electronic dictionaries are not.***
- ***Suggestion: if you spend 15 min / page \Rightarrow you'll have 30 min. extra to check your work.***

Mark breakdown:

Page 2. / 16
Page 3. / 12
Page 4. / 11
Page 5. / 12
Page 6. / 9
Page 7. / 12
Page 8. / 10
Page 9. / 8
Page 10. / 10
Page 11. / 5 *BONUS*

TOTAL: / 100 (MAXIMUM MARK = 105)

1. (___ / 16 marks) Circle the word(s) that correctly completes each of the following statements.

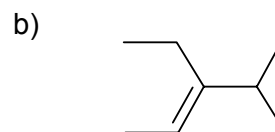
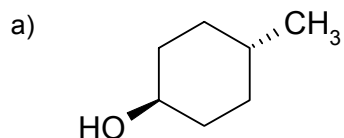
1 mark each:

- a) A molecule or atom that is described as electrophilic is also (LEWIS ACIDIC / LEWIS BASIC).
- b) If a bonding orbital and its corresponding antibonding orbital are both filled, the bond between the two atoms (FORMS / BREAKS).
- c) A radical species will be (STABILIZED / DESTABILIZED) by the presence of alkyl substituents on the atom carrying the unpaired electron.
- d) The rate of a reaction that occurs via an S_N2 mechanism will (DEPEND ON / NOT DEPEND ON) the concentration of the nucleophile.
- e) At room temperature, (SUFFICIENT / INSUFFICIENT) thermal energy is available for an alkene to rotate about its π -bond.
- f) A molecule with n stereogenic centres will have a maximum of ($2n$ / 2^n) stereoisomers.
- g) Markovnikov's rule works because electrophiles always add to the (MOST / LEAST) substituted sp^2 carbon in an alkene.
- h) Secondary alkyl halides react faster than primary alkyl halides in (S_N2 / E2) reactions.

2 marks each:

- i) A reaction pathway with a lower activation energy has a (MORE STABLE / LESS STABLE) transition state than another pathway with a higher activation energy.
- j) When an elimination occurs via the E1 mechanism, (ONLY ANTI / BOTH SYN AND ANTI) elimination products are observed.
- k) Any species whose conjugate acid has a pK_a (BELOW / ABOVE) the pK_a of another substance will be a strong enough base to deprotonate that substance.
- l) We would expect a tertiary amine to be (MORE SOLUBLE / LESS SOLUBLE) in water than a secondary amine with the same number of carbons.

2. (__ / 4 marks) Name the following molecules according to IUPAC conventions; include stereochemistry (*i.e.*, relative orientations and/or absolute configurations as appropriate).



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

a) (*R*)-3-ethoxy-2-methyloctane

b) *N,N*-dimethylcyclopentanamine

4. (__ / 4 marks) Draw structures that represent examples of each of the following types of compounds.

a) a primary amine

b) a meso compound

c) a secondary halide

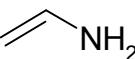
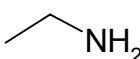
d) a polar aprotic solvent

5. (___/ 5 marks) Some properties of common alcohol solvents are listed in the table.

In which of these solvents would *t*-butyl bromide most rapidly undergo solvolysis (e.g., to form an ether product)? Explain your answer using a discussion of the reaction's mechanism.

Compound	Boiling point b.p. (°C)	Dielectric constant, ϵ (at 25°C)
CH ₃ OH	64.7	33
CH ₃ CH ₂ OH	78.3	25
(CH ₃) ₃ COH	82.3	11

6. (___/ 6 marks) For these questions, include any structural drawings that help clarify your explanations.

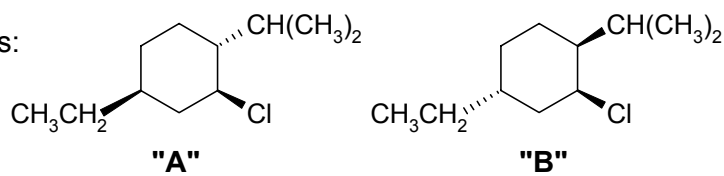
a) **(3 marks)** Which species is more acidic: vinylamine,  **or** ethylamine,  ?
Explain briefly.

b) **(3 marks)** Which species is the stronger nucleophile in a protic solvent: fluoride, F⁻ **or** iodide, I⁻ ?
Explain briefly.

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7. (___ / 12 marks) Molecules A & B are stereoisomers:



a) (2 marks) Are A & B diastereomers or enantiomers? How can you tell?

b) (3 marks) Draw the chair-chair interconversion (ring-flipping equilibrium) for each molecule.

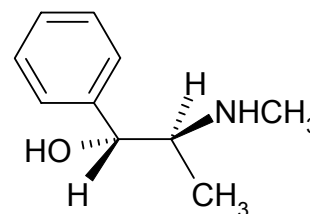
A:

B:

c) (2 marks) Circle the more stable chair conformation of each molecule.

d) (5 marks) Which molecule will undergo more rapid E2 elimination (under the same conditions)? Explain.

8. (9 marks) Ephedrine is a compound originally found in a Chinese herbal remedy for asthma that is now marketed as a drug. The stereoisomer shown here is the one that is active in causing the air passages in the lungs to dilate.



a) (1 mark) How many stereogenic carbons are present in this molecule?

b) (2 marks) Draw the molecule's enantiomer, and label its stereogenic carbons as *R* or *S* as appropriate.

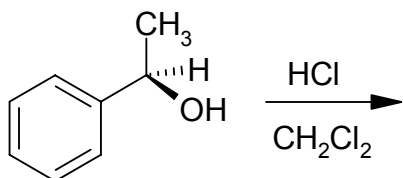
c) (2 marks) If the enantiomer shown is described as "levorotatory", in which direction will its enantiomer (*i.e.*, the molecule you drew in part (b)) rotate the plane of polarized light?

CIRCLE ONE: clockwise OR counterclockwise

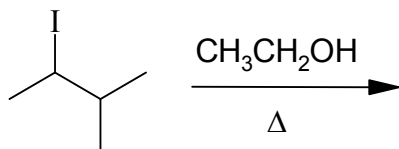
d) (4 marks) Imagine you prepare a sample of synthetic ephedrine in a pharmaceutical lab, and the compound must contain less than 0.5% of the (+) enantiomer in order to sell it as a drug. If a sample of pure (–) enantiomer yields a specific rotation of -10.0° , and your sample has an optical rotation of -9.5° , what percentage of the sample is composed of the (+) enantiomer? Is your sample pure enough to sell?

9. (/ 12 marks) REACTIONS: Predict the major product for **EACH** reaction; include stereochemistry.
(Note: read Question # 10 before you start this question).

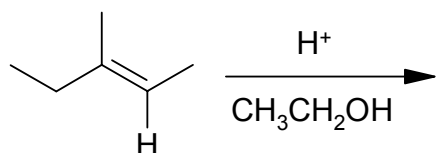
a) (3 marks) S_N2 reaction: (Note: if choosing this for Q.# 10, please include the S_N2 transition state)



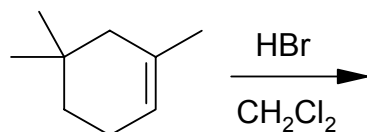
b) (3 marks) $E1$ reaction:



c) (3 marks) Acid-catalyzed addition of an alcohol:



d) (3 marks) Hydrobromination of an alkene:



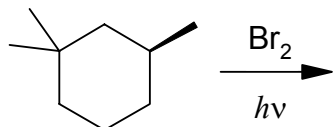
10. (/ 10 marks) MECHANISMS: For any TWO of the reactions from **Question # 9**, write complete step-by-step "arrow-pushing" mechanisms to explain how the predicted major product was formed. For each of your choices, please write the name of the reaction at the top of the mechanism.

(5 marks) CHOICE #1:

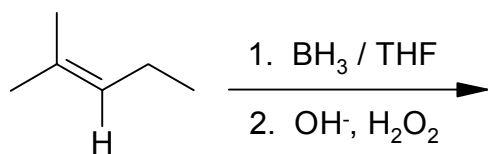
(5 marks) CHOICE #2:

11. (___ / 8 marks) REACTIONS: Predict the major product(s) for each reaction; include stereochemistry.

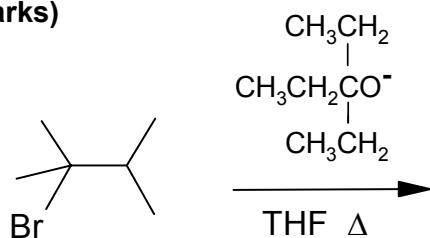
a) (2 marks)



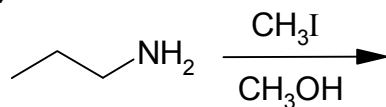
b) (2 marks)



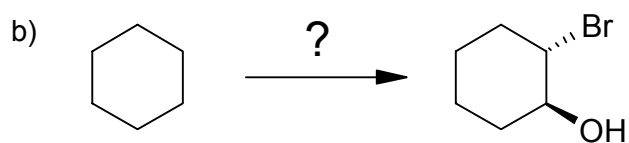
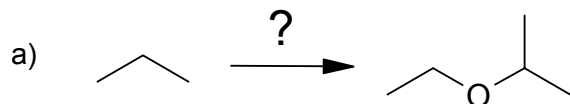
c) (2 marks)



d) (2 marks)



12. (/ 10 marks) CHOICE OF SYNTHESIS: Provide a 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 solvent type (protic vs. aprotic) and temperature (hot vs. cold).



BONUS QUESTION: (___/ 5 marks)

Imagine you have prepared a sample of racemic ephedrine (structure given in Question # 8). Describe the approach you would take to separate the enantiomers from each other. You do not need to provide a specific resolving agent, but you should describe what type of compound you would use and the explain chemistry involved in resolving the enantiomers.

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

pK_a VALUES

Compound	pK_a
CH ₃ CH ₂ CH ₂ CH ₃	>50
CH ₄	50
H ₂ C=CH ₂	44
RNH ₂	~40
NH ₃	36
HC≡CH	25
(CH ₃) ₃ COH	18
CH ₃ CH ₂ OH	16
CH ₃ OH	15.5
H ₂ O	15.7
RNH ₃ ⁺	~10
HCN	9
$\begin{array}{c} \text{OH} \\ \\ \text{CH}_3\text{C} \\ \\ \text{O} \end{array}$	4.7
HF	3.2
HN ₃	3
CH ₃ CH ₂ OH ₂ ⁺	-2.4
[CH ₃ CH ₂ OHCH ₂ CH ₃] ⁺	-3.6
H ₂ SO ₄	-5
HCl	-7
HI	-10