

COURSE	ORGANIC CHEMISTRY I	NUMBER	CHEM 221	SECTION	/2 01
EXAMINATION	Final Examination	DATE	December 20, 2005	TIME	1400-1700
INSTRUCTOR	Dr. Carrie ROGERS				

MATERIALS ALLOWED: NO YES (PLEASE SPECIFY) molecular model kits (without instructions)

CALCULATORS ALLOWED: NO YES programmable calculators must be "reset"

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 14 pages, including this cover page & a periodic table.***
- ***You may detach page containing the periodic table and pK_a 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).***
- ***Non-programmable calculators are allowed; cell phones & electronic dictionaries are not.***
- ***Suggestion: if spend 15 min / page (except bonus) \Rightarrow 30 min. extra to check your work.***

Mark breakdown:

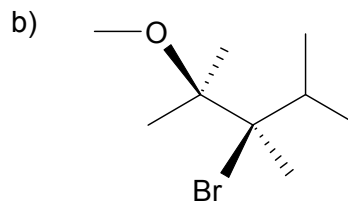
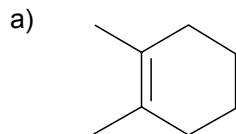
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Page 12. / 5 BONUS

TOTAL: / 100 (MAXIMUM MARK = 105)

1. (___ / 10 marks) Circle the word(s) that correctly completes each of the following statements:

- a) Electrophiles are strongly attracted to the π -electrons in alkenes and alkynes because π -electrons are relatively far from their atoms' nuclei and have high (ELECTRON DENSITY / POLARIZABILITY).
- b) To help favour elimination over substitution, chemists often (INCREASE / DECREASE) the reaction temperature, because elimination is a highly entropically favoured process whereas substitution is not.
- c) Simultaneous constructive and destructive interference of two atomic orbitals leads to the formation of one bonding molecular orbital and one (NONBONDING / ANTIBONDING) molecular orbital.
- d) The (POSITIVE FORMAL CHARGE / OPEN VALENCE) at the carbocationic center is what causes carbocations to be unstable, reactive intermediates.
- e) 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 MASS).
- f) S_N1 reactions typically follow a (ONE STEP / TWO-OR-MORE STEP) mechanism.
- g) 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.
- h) Cis and trans isomers of alkenes are examples of (STEREOISOMERS / CONFORMERS).
- i) The transition state of bimolecular elimination reaction resembles a(n) (CARBOCATION / ALKENE).
- j) Radical intermediates (CAN / CANNOT) stabilize themselves by undergoing rearrangements.

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



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

a) (Z)-2,3-diethylhept-2-en-1-ol

b) (S)-N-methyloctan-3-amine

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

a) a pair of diastereomers

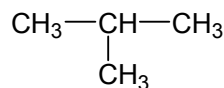
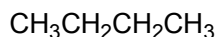
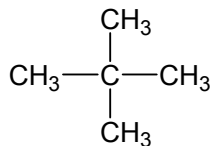
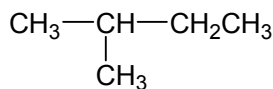
b) an allylic alcohol

c) a molecule with zero optical rotation

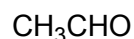
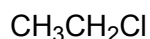
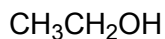
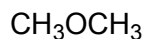
d) a molecule with two units of unsaturation

5. (8 marks) MULTIPLE CHOICE: Circle the correct choice.

- a) (2 marks) Which of the following molecules has the greatest van der Waals' interaction between molecules of the same kind?



- b) (2 marks) Which of the following substances would have the highest solubility in water?



- c) (2 marks) Which of the following describes the most stable conformation of trans-1-tert-butyl-3-methylcyclohexane?

- Both groups are equatorial.
- Both groups are axial.
- The *tert*-butyl group is equatorial.
- The *tert*-butyl group is axial.
- none of the above

- d) (2 marks) The S_N1 reaction between *tert*-butyl iodide and NaBr would be faster in acetone ($\epsilon = 21$) than in THF ($\epsilon = 7.6$) because:

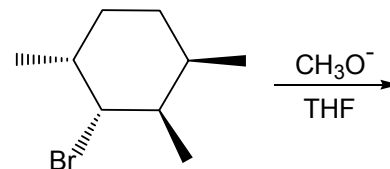
- the transition state of the rate limiting step has lower charge density than the reactants, so is stabilized more by a more polar solvent.
- the transition state of the rate limiting step has higher charge density than the reactants, so is stabilized more by a more polar solvent.
- the transition state of the rate limiting step has lower charge density than the reactants, so is stabilized more by a less polar solvent.
- the transition state of the rate limiting step has higher charge density than the reactants, so is stabilized more by a less polar solvent.
- none of the above.

6. (___/ 12 marks) For these questions, include drawings to support your explanations where appropriate.

- a) **(4 marks)** Which is more suitable for deprotonating diisopropylamine: NaNH_2 or $\text{CH}_3(\text{CH}_2)_2\text{CH}_2\text{Li}$? Explain your answer.
- b) **(4 marks)** Explain why *tert*-butoxide is a stronger base but a weaker nucleophile than ethoxide. Assume you are comparing their behaviour in the same solvent, e.g., THF.
- c) **(4 marks)** “*Markovnikov and anti-Markovnikov additions actually follow the same rules*”. To what is this statement referring, and why is it a helpful way to think?

7. (___ / 11 marks) Consider the following reaction mixture:

- a) (3 marks) Under the conditions shown, which TWO types of reaction could this molecule undergo? For each reaction, list the factors that allow you to predict which mechanism dominates.



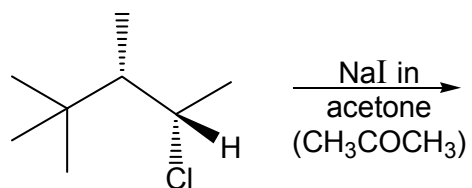
- b) (2 marks) Draw the MAJOR product, including stereochemistry, of each of the two reactions mentioned in part (a), and identify the mechanism from which each arises. [Note: Read part (c) now...].
- c) (6 marks) Justify why each product identified in part (b) forms, by summarizing the regiochemical, stereochemical and conformational requirements of the reaction's mechanism. You must include:
1. relevant conformational drawings, such as chair conformers and/or Newman projections
 2. electron-pushing arrows to show the mechanisms that lead to the two products
 3. a point-form list of relevant details beside each drawing (no paragraphs, please!)

8. (9 Marks) (S)-1-Chloro-2-methylbutane undergoes light-induced reaction with Cl_2 by a radical mechanism to yield a mixture of products. Among the products are 1,4-dichloro-2-methylbutane and 1,2-dichloro-2-methylbutane.

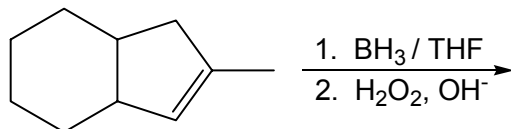
- a) **(3 marks)** Write an organic-style reaction equation, showing the structures of the reactants and the products named above. Include stereochemistry.
- b) **(2 marks)** One of the two products named above is optically active, but the other is optically inactive. Which is which, and why?
- c) **(4 marks)** Are the products shown in part (a) likely to be the major products of this reaction? If so, explain why, based on your understanding of the mechanism of the reaction. If not, briefly explain why not, and draw the structure(s) of the predicted major product(s).

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

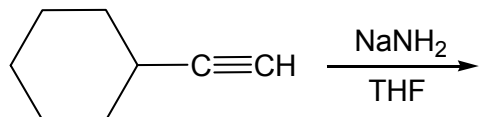
a) (2 marks)



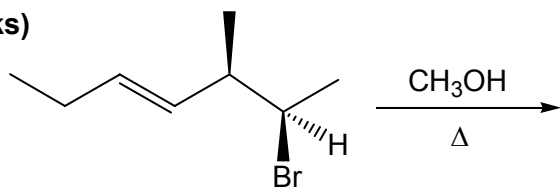
b) (2 marks)



c) (2 marks)

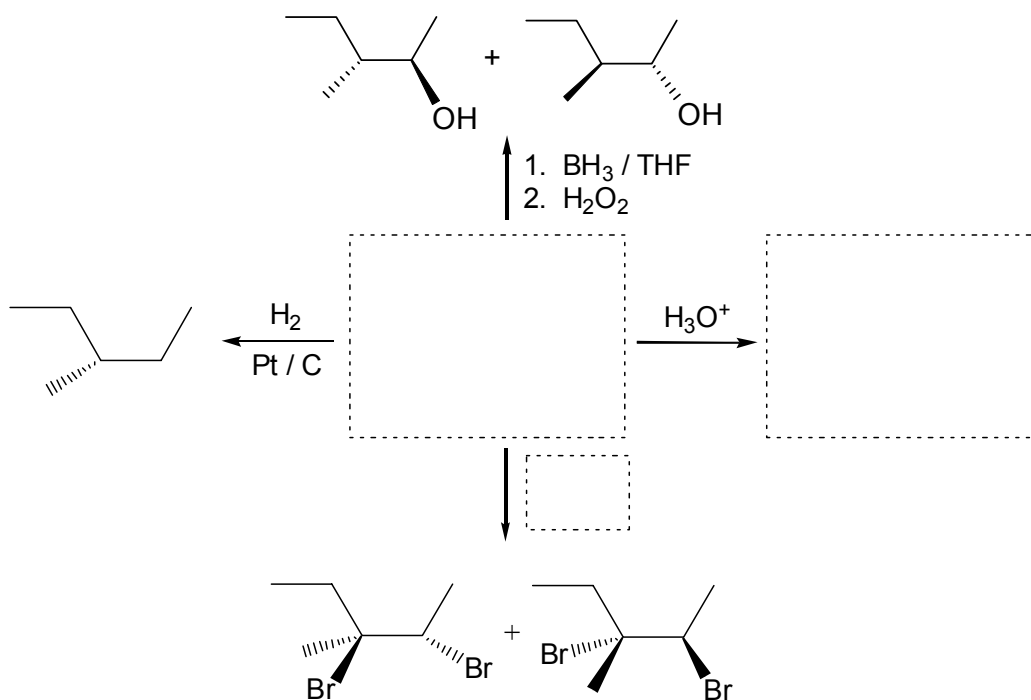


d) (2 marks)

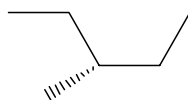


10. (/ 10 marks) REACTIONS and STEREOCHEMISTRY:

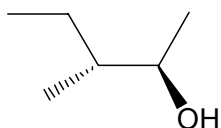
a) (5 marks) Identify the missing reactants, conditions and products marked by the dashed boxes.



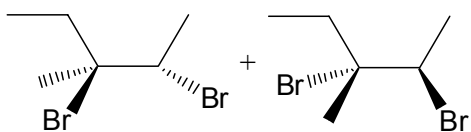
b) (5 marks) Answer the following questions about the stereochemistry of the compounds from part (a).



(i) Is this molecule chiral? Why or why not?



(i) Label the chiral center(s) in this molecule with an asterisk (*).
(ii) Provide the IUPAC name for this compound, including stereochemistry.

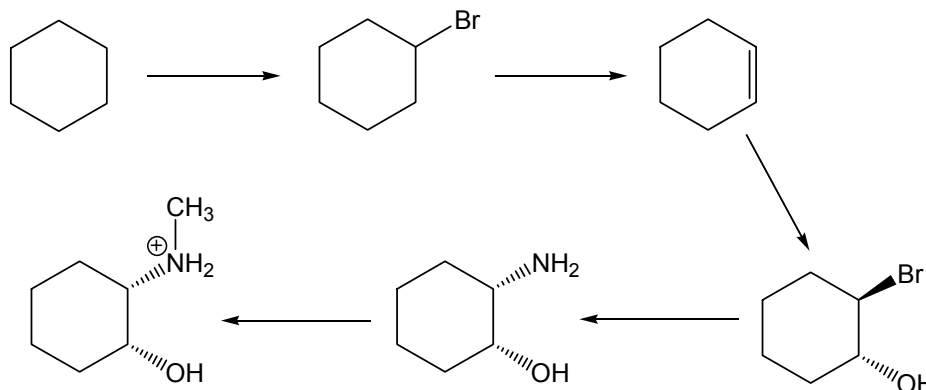


(i) What is the stereochemical relationship between these two compounds?

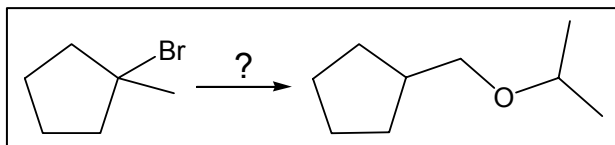
(ii) What conclusions, if any, can you make about the sign and/or magnitude of the specific rotation of these two compounds?

11. (___/ 10 marks) SYNTHESIS OF TARGET COMPOUNDS

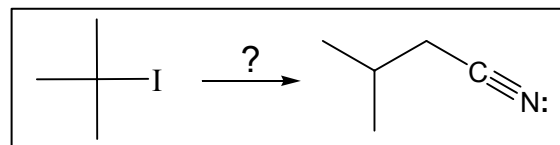
a) (5 marks) Above the arrow for **each** reaction, identify the reagents and conditions required to achieve the transformations shown.



b) (5 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 reaction conditions: relative concentrations (if important), solvent type, and temperature (hot vs. cold).
 [Note: If you do both synthesis, only the first one will be marked.]

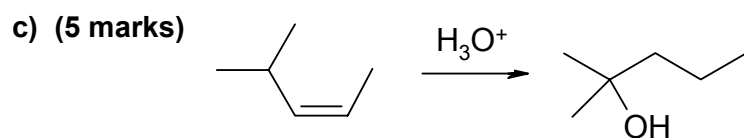
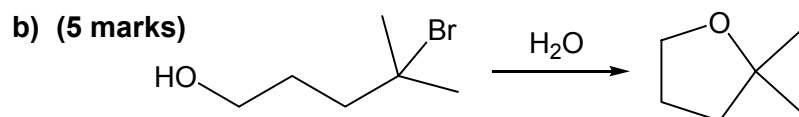
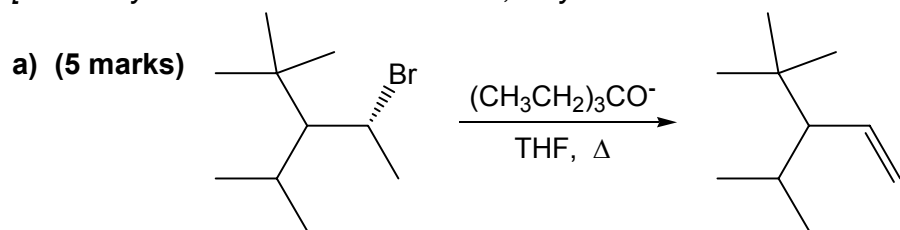


OR



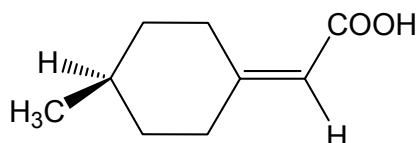
12. (/ 10 marks) MECHANISMS: Choose any **TWO** of the following reactions, and write complete step-by-step "arrow-pushing" mechanisms to explain how the product shown would be formed. If the reaction is a one-step process, you must include the structure of the transition state, labeled as [][‡].

[Note: If you do all three mechanisms, only the first two will be marked.]



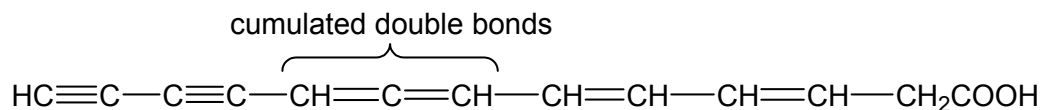
BONUS QUESTION: (___ / 5 marks)**For advance sitting:**

The structure of 4-methylcyclohexylideneacetic acid is shown below. It is a chiral molecule that does contain a chiral center, and was the first molecule of this type to be resolved into its two enantiomers. Explain why this molecule is chiral.

**For regular sitting:**

Allenes are a special class of alkenes that contain adjacent carbon-carbon double bonds, known as cumulated double bonds, as indicated below. Many allenes are chiral, even though they do not contain chiral carbon atoms. Mycomycin, for example, a naturally occurring antibiotic isolated from the bacterium *Nocardia acidophilus*, is chiral and has $[\alpha]_D = -130^\circ$. Why is mycomycin chiral? That is, what causes the chirality?

Drawing a 3-dimensional representation of the molecule should be helpful. To make the drawing simpler, assume the two conjugated (not cumulated) alkene units are of *trans* configuration (which has nothing to do with the chirality...).



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
H ₂	35
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