**THE UNIVERSITY OF CALGARY**

**FACULTY OF SCIENCE**

**MIDTERM  EXAMINATION**

**CHEMISTRY 351**

OCTOBER 28th 2003                                          Time: 2 Hours

**READ THE INSTRUCTIONS CAREFULLY**

PLEASE WRITE YOUR **NAME**, **STUDENT I.D. NUMBER** ON ***BOTH* YOUR ANSWER BOOKLET** AND **COMPUTER ANSWER SHEET**.

The examination consists of Parts 1 - 8, each of which should be attempted.  Note that some parts provide you with a choice of questions, *i.e.* answer 4 out of 5.  These will be graded in numerical order until the required number have been graded, regardless of whether they are right or wrong.  Parts 1 - 5 will be computer graded, and only Parts 6, 7, and 8 are to be answered in the booklet provided.  A periodic table with atomic numbers and atomic weights is located on the inside of this front cover.

Parts 1 - 5 consist of a series of multiple choice questions numbered 1 - 38 which are to be answered on your computer answer sheet. Indicate your answer by blackening out the appropriate space, A, B, C, D or E on the answer sheet.  Use a pencil only and ***not ink***.  In some cases it is required that you indicate ***multiple*** items for a complete and/or correct answer by blackening out more than one space.  In some other cases more than five options are available and some of these also require more than one space to be blackened out.  For an example, an option specified as AB requires that you blacken out ***both*** space A and space B.  Part marks may be awarded in some of the questions. Incorrect answers must be erased ***cleanly***.

Molecular models are permitted during the exam; calculators are also permitted, ***but NOT programmable calculators***.
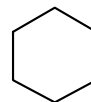
*16%* **PART 1    RELATIVE PROPERTIES**

**ANSWER ANY EIGHT (8) of questions 1-10  (2 marks per question)**

Arrange the items in **questions 1-10** in **DECREASING ORDER** (*i.e.* greatest, most etc. **first**) with respect to the indicated property.
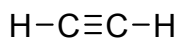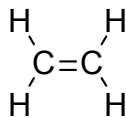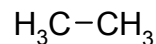
Use the following code to indicate your answers.

| | | | | |
|---|---|---|---|---|
| A. | i > ii > iii | | D. | ii > iii > i |
| B. | i > iii > ii | | E. | iii > i > ii |
| C. | ii > i > iii | | AB. | iii > ii > i |

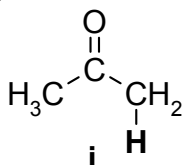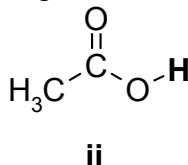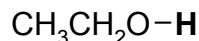1.  The **C-C-C** bond angle in each of the following molecules :
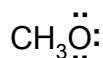
    

    **i**               **ii**               **iii**

2.  The amount of p-character in the hybridized orbitals in each of the following :

    $H-C\equiv C-H$          $\underset{H \quad\ H}{\overset{H \quad\ H}{C=C}}$          $H_3C-CH_3$

    **i**                    **ii**                    **iii**

3.  The acidity of the "**BOLD**" hydrogen in the following molecules :

         $CH_3CH_2O-\textbf{H}$

    **i** **H**                **ii**                **iii**

4.  The formal charge on the oxygen in each of the following molecules :

    $CH_3\ddot{\underset{..}{O}}:$          $CH_3CH_2\overset{..}{O}H_2$          $CH_3CH_2\overset{..}{\underset{..}{O}}CH_3$
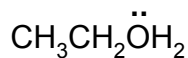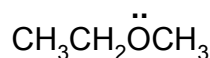
    **i**                    **ii**                    **iii**

5.  The number of constitutional isomers for each of the following molecular formulae:
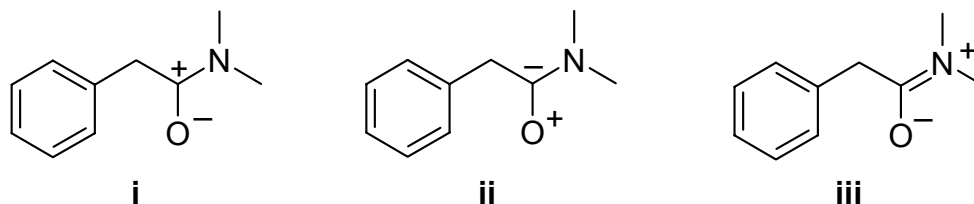
    $C_3H_6O$          $C_4H_8$          $C_5H_{12}$
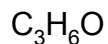
    **i**                **ii**                **iii**
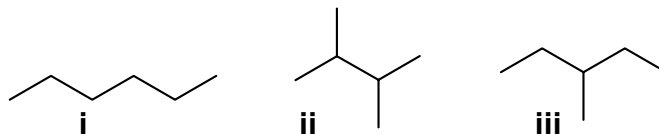
Use the following code to indicate your answers.

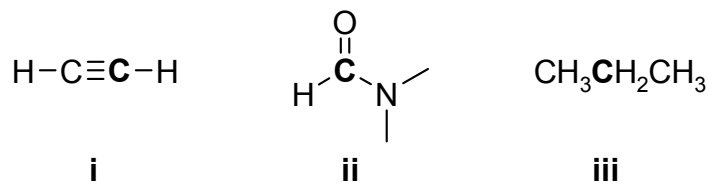| | | | |
|---|---|---|---|
| A. | i > ii > iii | D. | ii > iii > i |
| B. | i > iii > ii | E. | iii > i > ii |
| C. | ii > i > iii | AB. | iii > ii > i |

6. The relative importance of the following resonance contributors :



　　　　i　　　　　　　　　　　ii　　　　　　　　　　　iii

7. The relative stability of the following alkanes :



　　　　i　　　　　　　　　ii　　　　　　　　iii

8. Oxidation state of the "**BOLD**" carbons in each of the following molecules.

$$H-C\equiv \mathbf{C}-H$$



$$CH_3\mathbf{CH_2}CH_3$$

　　　　i　　　　　　　　　ii　　　　　　　　iii

9. The heat of combustion, $\Delta H_C°$, per methylene (-CH$_2$-) in each of the following (least exothermic to most exothermic):



　　　　i　　　　　　　　　ii　　　　　　　　iii
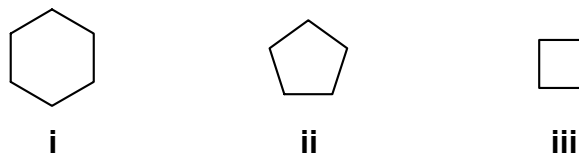
10. The relative energies of the following conformations of cyclohexane :

　　　chair　　　　　　　boat　　　　　　twist boat

　　　　i　　　　　　　　　ii　　　　　　　　iii
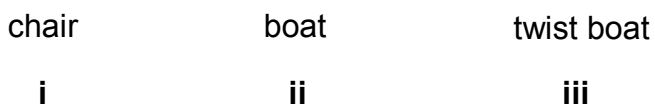
*9%*     **PART 2:   LABORATORY**

**ANSWER ALL of the questions 11-16 (1.5 marks per question).**

For questions 11-16, select the answer from those provided.  **If in some cases more than one answer may be correct, then all correct answers must be selected for full marks.**

11. Consider an extraction where the solute water / dichloromethane partition or distribution coefficient, $K_D$ = 1.   If you were to carry out the extraction using 1 g of solute in 100 mL of water, what % of the intial amount of solute will have been extracted after extraction and separation with 2 separate 50 mL portions of dichloromethane ?

    **A** 100 %     **B** 75 %     **C** 67 %     **D** 55 %     **E** 50 %

12. If the measured boiling point of a pure liquid sample in Calgary is 140$^o$C, then which of the following is closest to the boiling reported at sea level ?

    **A** 160 $^o$C     **B** 155 $^o$C     **C** 150 $^o$C     **D** 145 $^o$C     **E** 135 $^o$C

13. Which of the following experimental modifications would increase the separation efficiency of a fractional distillation experiment ?

    **A**  cooling the receiver flask
    **B**  increasing the flow of cooling water in the fractionating column
    **C**  using a longer fractionating column
    **D**  using a shorter fractionating column
    **E**  heating the distillation flask vigourously

14. Which of the following experimental methods would be **best** suited for the purification of a mixture of two miscible liquids ?

    **A** simple filtration          **B** vacuum filtration          **C** simple distillation
    **D** fractional distillation     **E** recrystallisation          **AB** evaporation

15. In experiment 8, the halogenation experiment investigating hydrocarbon reactivity, *t*-butylbenzene did not react with the bromine. This is because :

   **A**  it lacks a benzylic H and so can't form a stable radical
   **B**  it is too sterically hindered
   **C**  the branching makes it too stable
   **D**  bromine is too big to react with the benzene ring
   **E**  the resonance stabilised carbocation is so stable it doesn't react


16. If reaction of 0.92 g of toluene (IUPAC = methylbenzene) with 1.8 g of bromine gave 1.37 g of (1-bromomethyl)benzene, then what is the % yield of (1-bromomethyl)benzene ?

   **A** 149 %     **B** 80 %     **C** 76 %     **D** 66 %     **E** 54 %

*14%*   **PART 3:  MOLECULAR PROPERTIES**

**ANSWER ALL of the questions
17-23 (2 marks each)**

For each of the questions about
RAPAMYCIN (right), select the
answer from those provided.

**In some cases more than one
answer may be correct and for
full marks all correct answers
must be selected.**

**RAPAMYCIN**
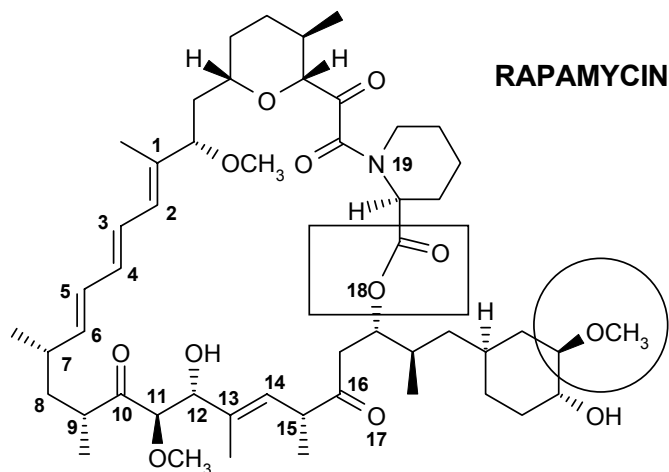
17.  What is the oxidation state of **C1**?

  **A**. −1         **B**. 0         **C**. +1         **D**. +2         **E**. +3

18.  What is the functional group in the circular box?

  **A**. ester      **B**. ketone      **C**. ether      **D**. alcohol      **E**. aldehyde

19.  What is the functional group in the rectangular box?

  **A**. ketone      **B**. ether      **C**. alcohol      **D**. ester      **E**. carboxylic acid

20.  How many units of unsaturation are there in Rapamycin?

  **A**. 10         **B**. 11         **C**. 12         **D**. 13         **E**. 14

21.  Which of the following atoms in Rapamycin  is / are **NOT** sp$^2$ hybridized?

  **A. C9**         **B. C10**         **C. O17**         **D. O18**         **E. N19**

22. Which of the following stereocentres in Rapamycin have an S-configuration?

  **A. C7**         **B. C9**         **C. C11**         **D. C12**         **E. C15**

23.  Which of the following alkenes are Z-alkenes ?

  **A. C1-C2**      **B. C3-C4**      **C. C5-C6**      **D. C13-C14**          **E. None**

*12%* **PART 4:  CONFORMATIONAL ANALYSIS**

**ANSWER ALL of the questions 24-29 (2 marks per question).**

For each of the **questions 24-29** select the answer from those provided.

24.  Which of the following terms **best** describes the position of the chloro-
     substituent in the conformation of *trans*-1-chloro-3-ethylcyclohexane shown
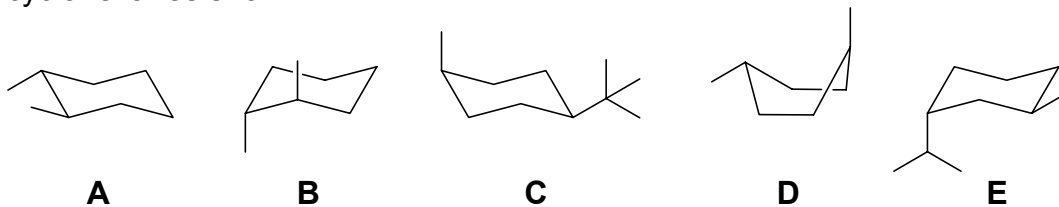     below?
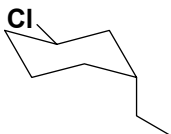


A  anti
B  axial
C  chair
D  equatorial
E  gauche

25.  Which of the following terms **best** describes the relationship between the
     **two methyl** groups in the conformation of butane shown in the Newman
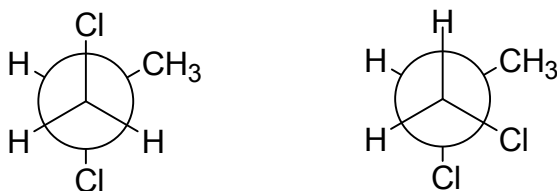     projection below ?
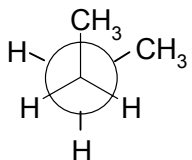


A  eclipsed
B  axial
C  gauche
D  anti
E  syn

26.  In which case(s) is/are the most stable conformation of the substituted
     cyclohexanes shown?



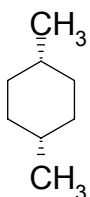A                    B                    C                    D                    E
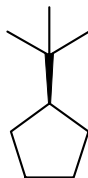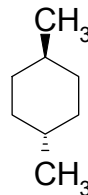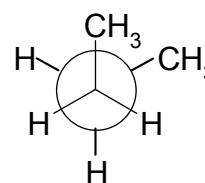
27. Which term **best** describes the isomer relationship between the two representations of 1,2-dichloropropane shown below ?



**A** cis    **B** trans    **C** constitutional    **D** conformational    **E** not isomers


28. In which of the molecules shown below would you expected the highest amount of torsional strain?



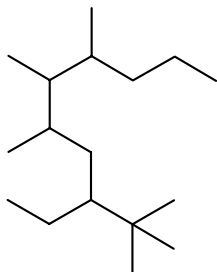    **A**          **B**          **C**          **D**          **E**


29. How many axial hydrogens does cis-1,2-dimethylcyclohexane have in its most stable conformation?

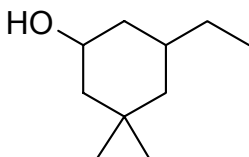    **A** 7        **B** 6        **C** 5        **D** 4        **E** 3

*14%*   **PART 5:   NOMENCLATURE**

**ANSWER ANY  SEVEN (7) of the questions 30-38 (2 marks per question).**

**For each of questions 30 to 34, select the correct name for the compound shown:**

30

**A**. 6-*t*-butyl-3,4-dimethyl-2-propyloctane
**B**. 2-ethyl-1,1,1,4,5,6-hexamethylnonane
**C**. 3-(1,1,1-trimethyl)-5,6,7-trimethyldecane
**D**. 3-ethyl-2,2,5,6,7-pentamethyldecane
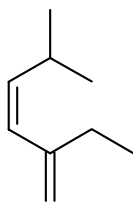**E**. 3-*t*-butyl-4,5,6-trimethyldecane

31

**A**. 5-ethyl-3,3-dimethylphenol
**B**. 3-ethyl-5,5-dimethylphenol
**C**. 5-ethyl-3,3-dimethylcyclohexanol
**D**. 3,3-dimethyl-5-ethylcyclohexanol
**E**. 5-ethyl-3,3-dimethylhexanol

32
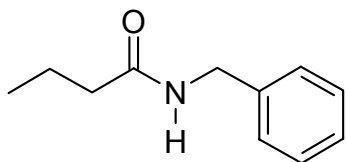
**A**. N-benzyl butanamine
**B**. N-phenyl butanamine
**C**. N-benzyl butanamide
**D**. N-phenyl butanamide
**E**. *n*-butyl benzylamine

33

**A**. (Z)-3,6-dimethyl-3,4-heptadiene
**B**. (Z)-1-isopropyl-3-ethyl-1,3-butadiene
**C**. (Z)-2-ethyl-5-methyl-1,3-hexadiene
**D**. (E)-5-ethyl-2-methyl-1,3-hexadiene
**E**. (Z)-3-ethyl-1-isopropyl-1,3-butadiene

34
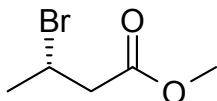
**A**. methyl  (S)-3-bromobutanoate
**B**. methyl  (S)-3-bromobutyl methyl ether
**C**. (R)-2-bromobutanoate
**D**. (S)-2-bromobutanoate
**E**. ethyl  3-bromobutanoate

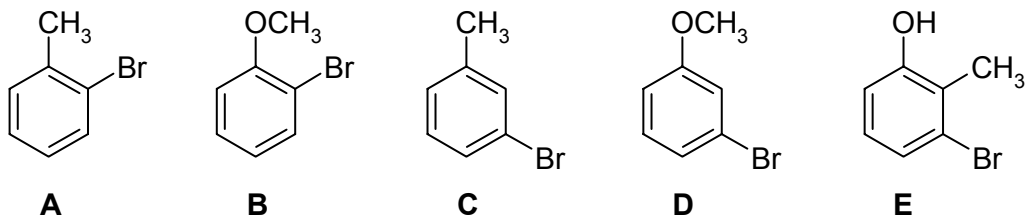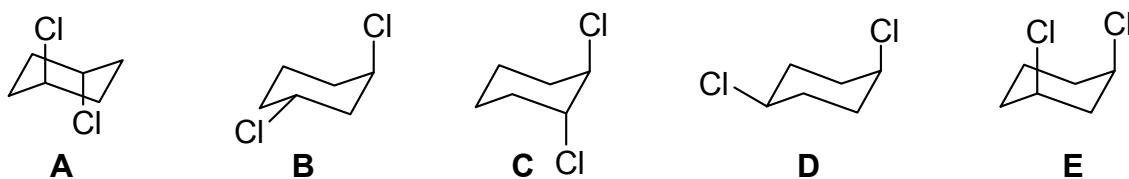**For each of questions 35 to 38, select the correct structure for the name provided:**

35.  *ortho*-bromomethoxybenzene

|  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: |
| A | B | C | D | E |

36.  *cis* 1,3-dichlorocyclohexane :

|  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: |
| A | B | C | D | E |

37.  (S)-3-hydroxy-4-pentenal :

|  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: |
| A. | B. | C. | D. | E. |
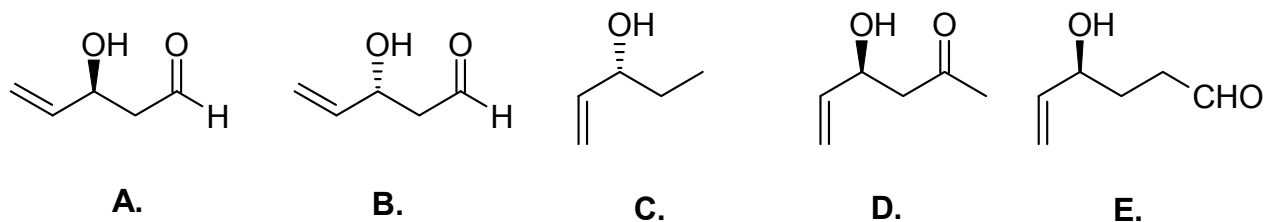
38.  2-methylbicyclo[2.2.2]oct-2-ene:

|  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: |
| A | B | C | D | E |
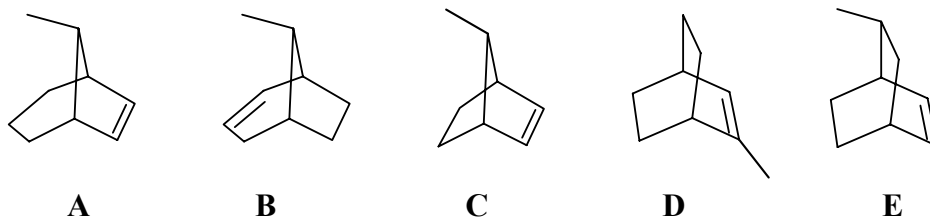
*11%*   **PART 6:   STRUCTURE DETERMINATION**:

**Write your answer in the booklet provided.  For FULL marks you MUST show your working.  PARTIAL marks will be awarded.**

**THE QUESTIONS IN THIS SECTION SHOULD ALL BE ANSWERED BASED ON THE FOLLOWING DATA:**

An elemental analysis (via combustion analysis in oxygen) was performed on a sample taken from an unlabelled drum found abandoned at a former industrial area. The result indicated that the sample contained 66.63% C and 11.18% H by weight. Spectroscopic analysis showed the sample molecular weight to be 72.107 g/mol

(a)  Determine the molecular formula.

Using **this molecular formula** draw :

(b)  4 different functional groups that may be found in compounds with this formula

(c) a pair of constitutional isomers

(d) a pair of enantiomers and give their complete IUPAC names

*12%*   **PART 7: MECHANISM**

**Write your answer in the booklet provided.**

**Draw a mechanistic sequence** using double headed (*i.e.* electron pair) curly arrows that represents the ***single reaction sequence*** described verbally by the following points in which 1-phenylpropanol is dehydrated to give E-1-phenyl-1-propene.

*Step 1:*  An acid-base reaction where 1-phenylpropanol is protonated by sulfuric acid to give an oxonium ion.

*Step 2:* Loss of a water molecule from this species creating a resonance stabilized carbocation.

*Step 3:*  Using B: as base, remove a proton from an $sp^3$ hydridized carbon atom in the carbocation to give E-1-phenyl-1-propene as the major product.

Draw the **four major** resonance contributors to the structure of the carbocation formed in Step 2.  You should use curly arrows to illustrate how you move between the resonance structures.

Given that the heats of combustion, $\Delta H_C^o$, of E-1-phenyl-1-propene  = -1146.5 kcal/mol and Z-1-phenyl-1-propene = -1157.5 kcal/mol suggest a reason why the E isomer is the major product.

What type of isomers are E- and Z-alkenes **best** described as ?

*12%*  **PART 8:   THERMODYNAMICS**

**Write your answer in the booklet provided.  Show your working as PARTIAL marks will be given.**

There are two configurational isomers of 1,2-dimethylcyclohexane. Isomer **I** has a heat of combustion, $\Delta H_C^o$ of -1248.8 kcal/mol, and isomer **II** has a heat of formation, $\Delta H_f^o$, of +32 kcal/mol.

Given that the heats of combustion for graphite, $\Delta H_C^o$, C (graphite) = -94.05 kcal/mol and for hydrogen, $\Delta H_C^o$ $H_2$ (gas) = -57.8 kcal/mol, calculate :

i. $\Delta H_f^o$, for isomer **I**

ii, $\Delta H_C^o$, for isomer **II.**

Which isomer is more stable ?

Rationalise this based on an analysis of the conformations.

# ** THE END **