

THE UNIVERSITY OF CALGARY
FACULTY OF SCIENCE
MIDTERM EXAMINATION
CHEMISTRY 351

November 2nd, 2005

Time: 2 Hours

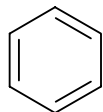
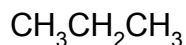
READ THE INSTRUCTIONS CAREFULLY

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 inside the front cover.

Parts 1 - 5 consist of a series of multiple choice questions numbered 1 - 40 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**B.** i > iii > ii**C.** ii > i > iii**D.** ii > iii > i**E.** iii > i > ii**AB.** iii > ii > i1. The **C-C-C** bond angles in each of the following molecules :**i****ii****iii**2. The relative strength of the **C-H bonds** in each of the following :

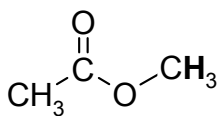
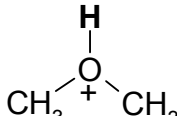
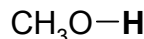
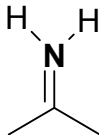
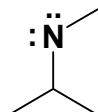
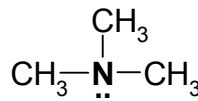
ethane

i

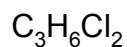
cyclohexane

ii

ethyne

iii3. The acidity of the "**BOLD**" hydrogen in the following molecules :**i****ii****iii**4. The formal charge on the **nitrogen atom** in each of the following molecules :**i****ii****iii**

5. The number of isomers (excluding conformational isomers) of the following molecules.

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

Use the following code to indicate your answers.

A. $i > ii > iii$

B. $i > iii > ii$

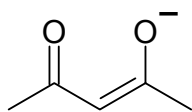
C. $ii > i > iii$

D. $ii > iii > i$

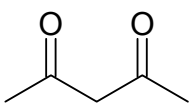
E. $iii > i > ii$

AB. $iii > ii > i$

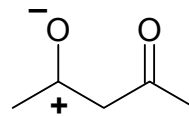
6. The relative importance of the following resonance contributors :



i

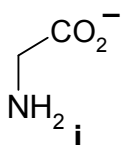


ii

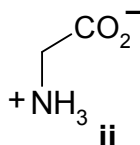


iii

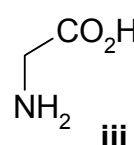
7. The relative amounts of the following produced when an aqueous solution of the amino acid glycine is reacted with 1 mole equivalent of NaOH:



i

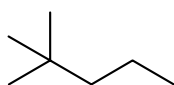


ii

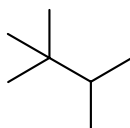


iii

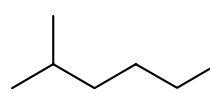
8. The relative heats of formation of the following alkanes (least exothermic to most exothermic):



i

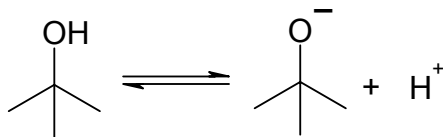


ii

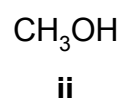


iii

9. The relative amount of the conjugate base (*i.e.* t-butoxide) formed by the reaction of 1 mole equivalent of each of the following with t-butanol:



i

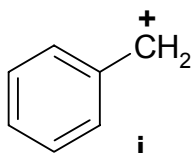


ii

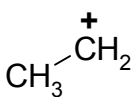


iii

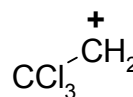
10. The relative stabilities of the following carbocations :



i



ii



iii

9% PART 2: LABORATORY

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

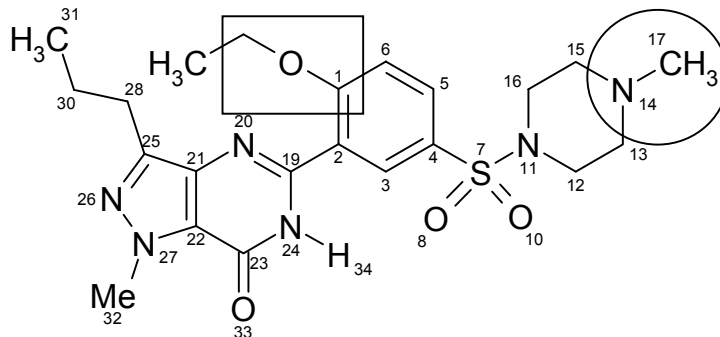
For questions 11-16, select the apparatus for most efficiently carrying out the required task from the list provided:

11. Separate a mixture containing 50 mL of water & 50 mL of dichloromethane
12. Remove a solid impurity from a liquid
13. Check the purity of a solid sample
14. Collect crystals from the mother liquor
15. Separate a mixture of 50 mL of water & 50 mL of ethanol
16. Isolate an organic solid that is dissolved in a dichloromethane solution

- A** Cold Finger
- B** Distillation Apparatus
- C** Filtering Funnel
- D** Fischer-Johns Apparatus
- E** Gas-Liquid Chromatograph
- AB** Graduated Pipette
- AC** Hirsch Funnel
- AD** Rotary Evaporator
- AE** Separatory Funnel
- BC** Thin Layer Chromatography Plate

16% **PART 3: MOLECULAR PROPERTIES****ANSWER ALL of the questions 17-24**

In the year of its launch, VIAGRA® (right) was used by over three million satisfied customers. Each of the questions below refers to the structure of VIAGRA® - select the answer(s) from the options provided.



17. What are the oxidation state of **C13** and **N26** ?

- A. -1, -2 B. +1, -2 C. -1, +3 D. -1, -3 E. +1, -3

18. What is the functional group in the circle?

- A. amide B. amine C. aniline D. nitrile E. nitro

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

- A. alcohol B. epoxide C. ester D. ether E. phenol

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

- A. 7 B. 8 C. 11 D. 12 E. 13

21. In VIAGRA, what are the hybridisations of **O10**, **N14** and **N20** respectively?

- A. sp^3 , sp^3 , sp^3 B. sp^2 , sp^3 , sp^3 C. sp^3 , sp^2 , sp^3
 D. sp^2 , sp^3 , sp^2 E. sp^2 , sp^2 , sp^2 AB. sp^2 , sp^2 , sp

22. In VIAGRA, what are the hybridisations of **C2**, **C3** and **N24** respectively?

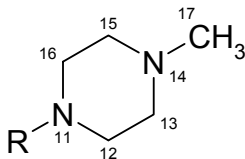
- A.** sp^3 , sp^3 , sp^3 **B.** sp^2 , sp , sp^3 **C.** sp^3 , sp^2 , sp^3
D. sp^3 , sp^3 , sp^2 **E.** sp^2 , sp^2 , sp^3 **AB.** sp^2 , sp^2 , sp^2

23. How many carbon chiral centres are there in VIAGRA ?

- A.** 0 **B.** 1 **C.** 2 **D.** 3 **E.** 5

24. In the most stable conformation of the six-membered heterocyclic ring (see below), how many hydrogen atoms would be found in axial positions ?

- A.** Zero – the equatorial position is always more stable
B. Zero – the most stable conformation of this ring is planar
C. 2
D. 4
E. 6

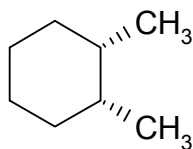


12% **PART 4: CONFORMATIONAL ANALYSIS**

ANSWER ALL of the questions 25-32 (1.5 marks per question).

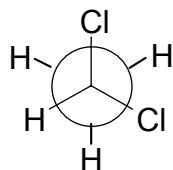
For each of the **questions 25-32** select the answer(s) from those provided. In some cases more than one answer may be correct in which case all correct answers should be selected for full marks.

25. What is the torsional angle between the two methyl groups in the most stable conformation of the substituted cyclohexane shown below?



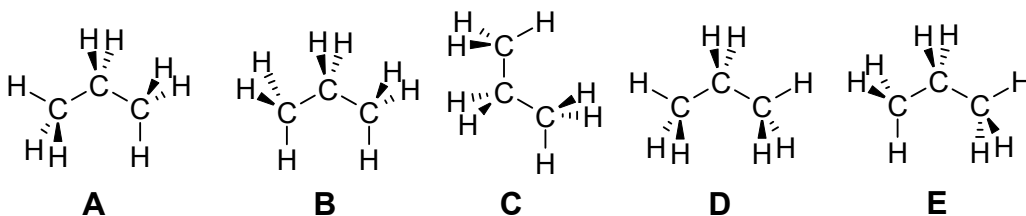
- A** 0° **D** 109.5°
B 60° **E** 120°
C 90° **AB** 180°

26. Which of the following terms **best** describes the conformation shown in the Newman projection below ?



- A** eclipsed **D** gauche
B staggered **E** syn
C anti **AB** trans

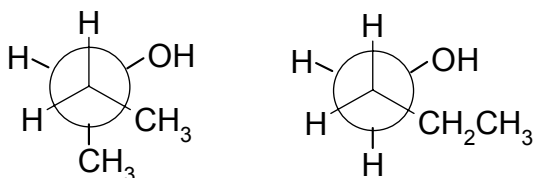
27. Which of the following diagrams represent the most stable conformation for propane ?



28. Which of the following is / are isomers of 2-ethoxypropene ?

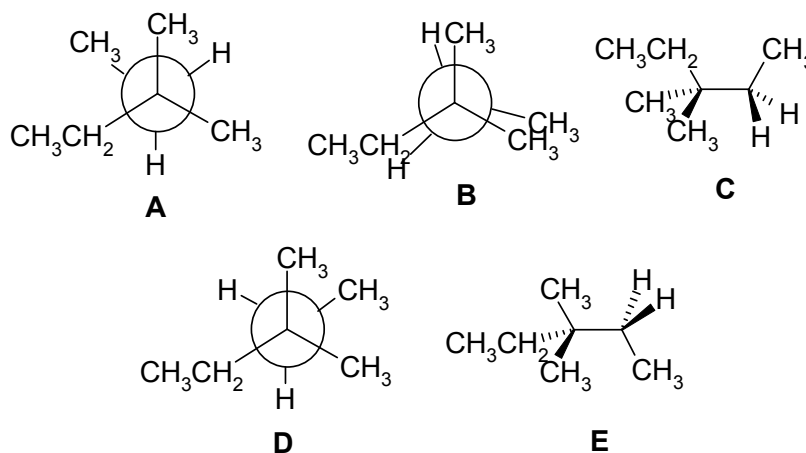
- A** 2-pentanol **B** 2-methylbutanal **C** 2-pentanone
D (Z)-1-ethoxy-1-propene **E** cyclopentanol

29. Which of the following terms **best** describes the relationship between the two molecules shown below ?



- A** constitutional isomers
B stereoisomers
C configurational isomers
D conformational isomers
E enantiomers
AB they are the same molecule

30. Which of the following conformations of 3,3-dimethylpentane is the most stable?



31. Which of the following is the **best** example of Van der Waals strain?

- A** the C-C-C bond angles in cyclopentane
B the strain in the eclipsed conformation of 2,2,3,3-tetramethylbutane
C the flagpole interaction in the boat conformation of cyclohexane
D the alignment of the C-C bonds in cyclobutane
E the strain in cyclobutane compared to butane

32. Which of the following shows the correct relative energy order for the conformations of butane?

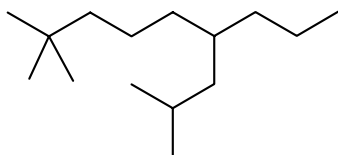
- A** anti > gauche > syn
B anti > syn > gauche
C gauche > syn > anti
D gauche > anti > syn
E syn > anti > gauche
AB syn > gauche > anti

14% **PART 5: NOMENCLATURE**

ANSWER ANY SEVEN (7) of the questions 33-40 (2 marks per question).

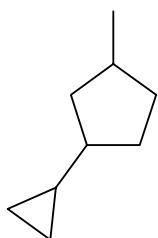
For each of questions 31 to 34, select the correct name for the compound shown:

33



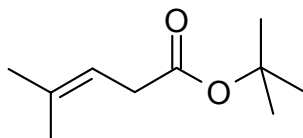
- A. 6-propyl-2,2,8-trimethylnonane
- B. 6-isopropyl-2,2-dimethylnonane
- C. 6-butyl-2,2,8-methylnonane
- D. 2,8,8-trimethyl-4-propylnonane
- E. 2,2,8-trimethyl-6-propylnonane

34



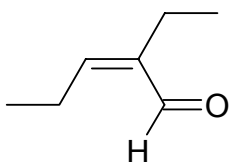
- A. 3-cyclopropyl-1-methylcyclopentane
- B. 1-methyl-3-cyclopropylcyclopentane
- C. 1-cyclopropyl-4-methylcyclopentane
- D. 1-propyl-3-methylcyclopentane
- E. 1-cyclopropyl-3-methylcyclopentane

35



- A. isobutyl 4-methylpent-3-enoate
- B. isobutyl 2-methylpentenoate
- C. t-butyl (Z)-4-methylpent-3-enoate
- D. t-butyl (E)-4-methylpent-3-enoate
- E. t-butyl 4-methylpent-3-enoate

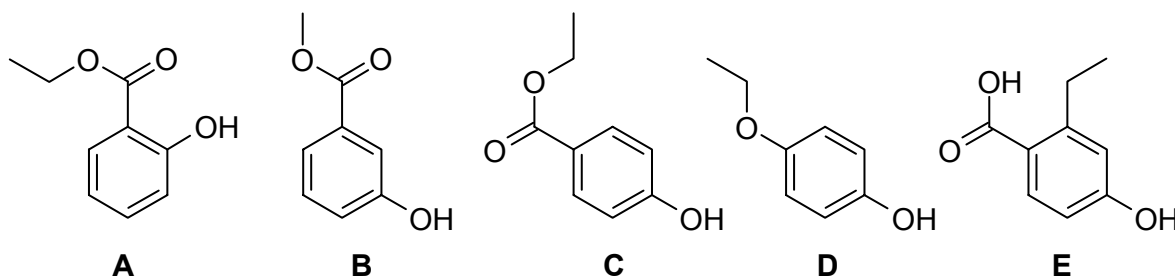
36



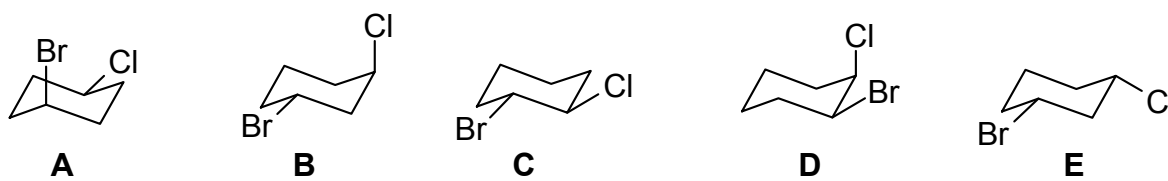
- A. *trans*-hex-3-enal
- B. (Z)-hex-3-enol
- C. (Z)-2-ethylpent-2-enal
- D. (Z)-2-ethylpent-2-enone
- E. (E)-2-ethylpent-2-enal

For each of questions 37 to 40, select the correct structure for the name provided:

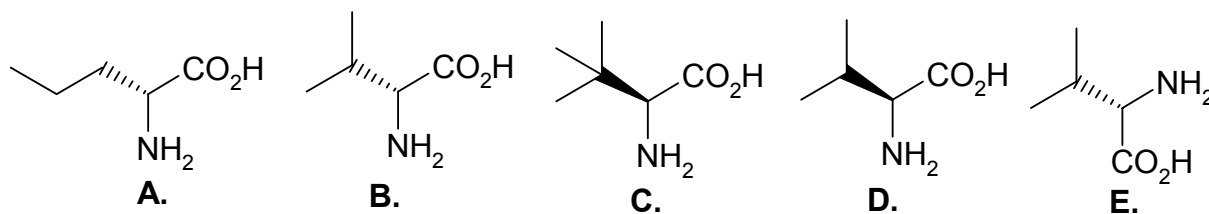
37. ethyl *para*-hydroxybenzoate



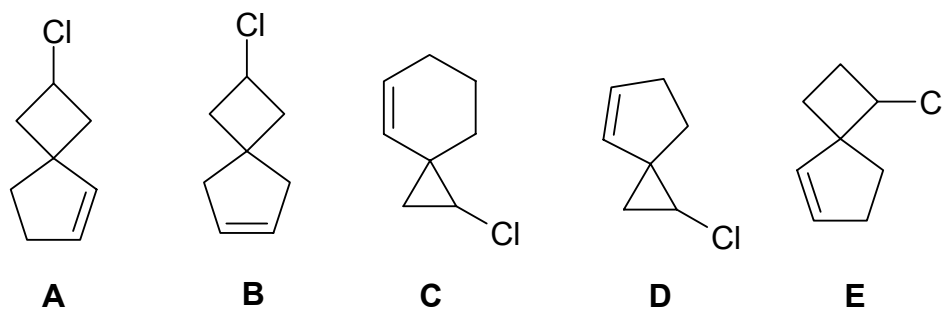
38. *cis* 1-bromo-3-chlorocyclohexane :



39. (*R*)-2-amino-3-methylbutanoic acid :



40. 2-chlorospiro[3.4]oct-5-ene:



10% PART 6: STRUCTURE DETERMINATION:

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

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

Analysis was performed on a sample taken from an unlabelled drum found in a derelict warehouse. The sample was determined to be a single compound by gas chromatography and analysis indicated that the molecule contained 4 carbon, 2 oxygen and 8 hydrogen atoms.

- (a)** Determine the molecular mass of this molecule
- (b)** What is the IHD of this molecule? (IHD = index of hydrogen deficiency)
- (c)** Name **five** different functional groups that may be found in compounds with this molecular formula
- (d)** Draw two constitutional isomers and give their complete IUPAC names
- (e)** Draw a pair of enantiomers
- (f)** If the molecule in the drum was found to contain only one type of carbon, one type of hydrogen, and one type of oxygen, what is the structure?

12% **PART 7: MECHANISM**

Write your answer in the booklet provided.

(a) 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 the ester, methyl propanoate, undergoes alkylation to give a new ester, methyl 2-methylpropanoate when reacted with a base and then an alkylating agent.

Step 1. An acid - base reaction in which a proton is removed from the methyl propanoate using the base, sodium amide, to create a resonance stabilized carbanion and ammonia.

Step 2. Attack of the carbanion (as a nucleophile) on the electrophilic carbon of methyl iodide causing the simultaneous loss of an iodide ion and forming a new C-C sigma bond to give methyl 2-methylpropanoate.

(b) Also answer the following questions :

- (i) Draw the significant resonance contributor(s) for the carbanion formed from methyl propanoate
- (ii) The pKa for the H atom removed in methyl propanoate is about 25, yet in propane the pKa is over 50. Briefly explain why there is such a large difference in acidity.
- (iii) Based on the information provided in this question, what alkylating agent should you use if you wanted to prepare methyl 2-methylhexanoate from methyl propanoate ?

12% **PART 8: THERMODYNAMICS**

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

Consider the following four compounds:

- I cycloheptane
- II ethylcyclopentane
- III *cis*-1,3-dimethylcyclopentane
- IV 1,1,2,2-tetramethylcyclopropane

- (a) (i) Draw the structures I - IV
(ii) Which of these structures are isomers?
(iii) What type of isomers are they?
- (b) Given that the heats of combustion for graphite, ΔH_C° , C (graphite) = -93.9 kcal/mol and for hydrogen, ΔH_C° H₂ (gas) = -68.4 kcal/mol, and the heat of combustion of cycloheptane = -1098.8, **calculate ΔH_f° , for cycloheptane.**
- (c) The other three structures have the following heats of formation.

$$\Delta H_f^\circ = -28.6 \text{ kcal/mol}$$

$$\Delta H_f^\circ = -40.2 \text{ kcal/mol}$$

$$\Delta H_f^\circ = -39.1 \text{ kcal/mol}$$

- (i) match the compounds II - IV to their corresponding ΔH_f° values
(ii) of the compounds I - IV which is the most stable?
(iii) of the compounds I - IV which is the least stable?
- (d) What are the main factors that affect the stability of alkanes and cycloalkanes? Briefly state how these factors can be used to assign the values in **part c (i)**

**** THE END ****