

THE UNIVERSITY OF CALGARY
FACULTY OF SCIENCE
MIDTERM EXAMINATION
CHEMISTRY 351

November 3rd, 2004

Time: 2 Hours

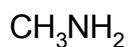
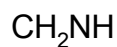
READ THE INSTRUCTIONS CAREFULLY

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 **H-C-N** 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 :

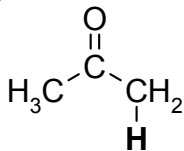
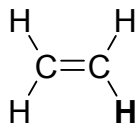
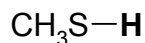
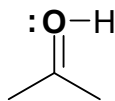
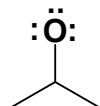
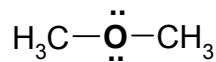
ethane

i

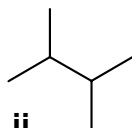
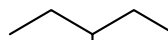
ethene

ii

ethyne

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

5. The relative boiling points of the following alkanes :

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

Use the following code to indicate your answers.

A. i > ii > iii

B. i > iii > ii

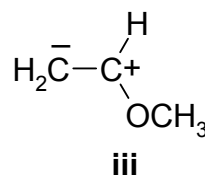
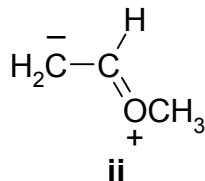
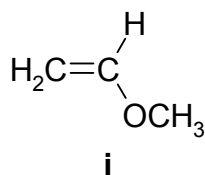
C. ii > i > iii

D. ii > iii > i

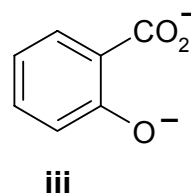
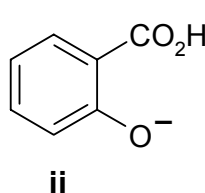
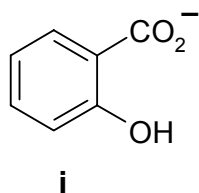
E. iii > i > ii

AB. iii > ii > i

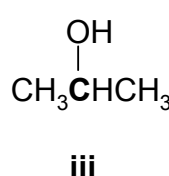
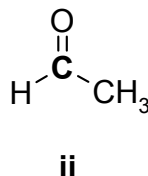
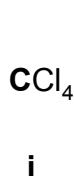
6. The relative importance of the following resonance contributors :



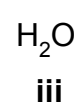
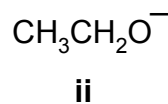
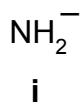
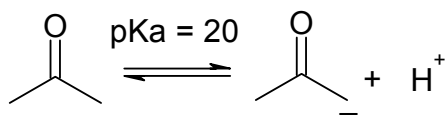
7. The relative amounts of the following produced when salicylic acid (also called *ortho*-hydroxybenzoic acid) is reacted with 1 mole equivalent of NaOH:



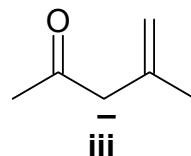
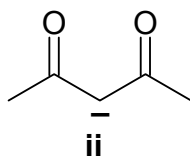
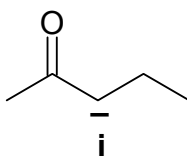
8. Oxidation state of the “**BOLD**” carbons in each of the following molecules.



9. The relative amount of the conjugate base formed (an enolate) by the reaction of 1 mole equivalent of each of the following with acetone :



10. The relative stabilities of the following carbanions :



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.**

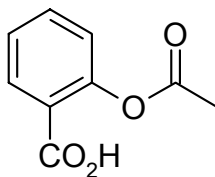
11. Consider an extraction where the solute partition or distribution coefficient, $K_D = 2$ for chloroform : water. If you were to carry out the extraction using 1g of solute in 50 mL of water, what % of the initial amount of solute will have been extracted after extraction and separation with 2 separate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

A 100 % B 89 % C 75 % D 67 % E 50 %

12. If the measured boiling point of a pure liquid sample here in Calgary is 200°C , then which of the following is closest to the correct value at sea level ?

A 190°C B 195°C C 200°C D 205°C E 210°C

13. If reaction of 1.38 g of salicylic acid (IUPAC = ortho-hydroxybenzoic acid) with 1.0 g acetic anhydride (IUPAC = ethanoic anhydride) gave 1.2 g of aspirin (see below), then what is the percentage yield of aspirin ?

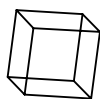


A 87 % B 83 % C 67 % D 52 % E 50 %

14. How many types of hydrogen and carbon are there in 1,2-diethylbenzene?

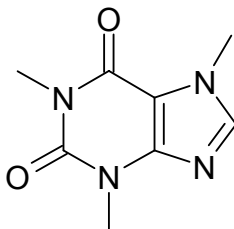
A 3H, 4C B 3H, 5C C 4H, 4C
D 4H, 5C E 5H, 4C AB 5H, 5C

15. What is the index of hydrogen deficiency (IHD) of benzene and cubane respectively ?



cubane

- A** 3 & 4 **B** 4 & 4 **C** 3 & 5 **D** 3 & 6 **E** 4 & 6 **AB** 4 & 5
16. Which of the following statements from the extraction of caffeine experiment is/are true ?
- A** The dichloromethane solution was washed with NaOH to remove acidic impurities such as tannic acid
 - B** Magnesium sulphate was used to remove coloured impurities
 - C** Petroleum ether is used during recrystallisation to lower the polarity of the solvent
 - D** Acetone was used during recrystallisation since it is polar enough to dissolve caffeine
 - E** Caffeine has the structure shown below

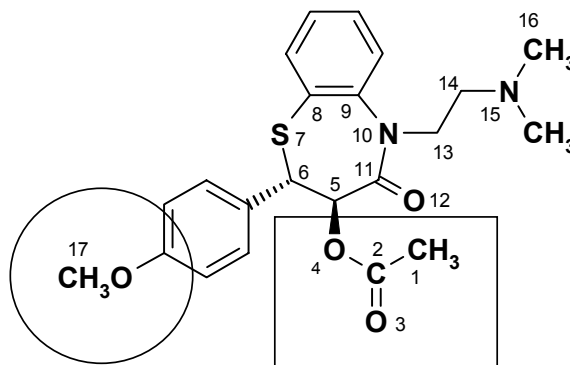


14% **PART 3: MOLECULAR PROPERTIES**

ANSWER ALL of the questions 17-24

For each of the questions about DILTIAZEM® (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.



17. What are the oxidation state of **C2** and **C13** ?

- A. +4,-1 B. +3,+1 C. +3,-1 D. +2, -1 E. -3,-1

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

- A. aldehyde B. ester C. ketone D. ether E. carboxylic acid

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 DILTIAZEM ?

- A. 8 B. 9 C. 10 D. 11 E. 13

21. In DILTIAZEM, what are the hybridisations of **O12**, **N10** and **N15** respectively?

- A. sp^3 , sp^3 , sp^3 B. sp^2 , sp^3 , 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

22. In DILTIAZEM, what are the hybridisations of **C2**, **C5** and **C17** respectively?

- A.** sp^3 , sp^3 , sp^3 **B.** sp^2 , sp^3 , 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. Which of the following describes the absolute configurations at C5 and C6 ?

- A.** R,R **B.** R,S **C.** S,R **D.** S,S **E.** trans

24. In DILTIAZEM, which of the following atoms is the most basic ?

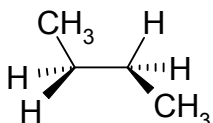
- A.** O4 **B.** C8 **C.** N10 **D.** N15 **E.** C17

12% **PART 4: CONFORMATIONAL ANALYSIS**

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

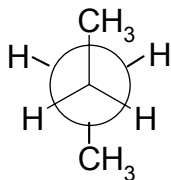
For each of the **questions 25-32** select the answer(s) from those provided.

25. Which of the following terms **best** describes the conformation of butane shown below?



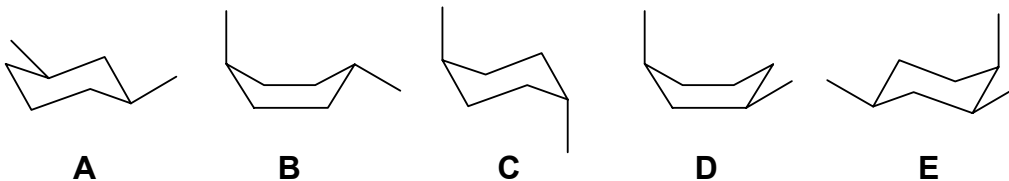
- A** anti
B eclipsed
C gauche
D staggered
E syn
AB twist or skew

26. 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 staggered
C anti
D gauche
E syn
AB trans

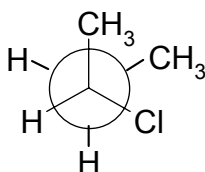
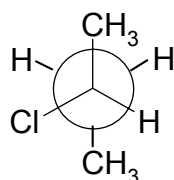
27. Which of the following diagrams represent the most stable conformation for the relevant substituted cyclohexane ?



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

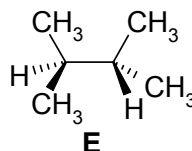
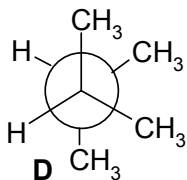
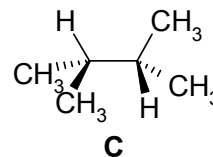
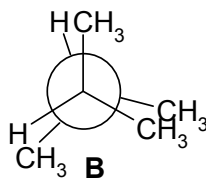
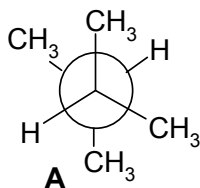
- A** 2-butanol **B** diethyl ether **C** butanal
D butanoic acid **E** cyclopropylmethanol

29. Which term **best** describes the relationship between the two representations of 2-chlorobutane shown below ?



- A** constitutional
B stereoisomers
C configurational
D conformational
E enantiomers
AB not isomers

30. Which of the following represents the most stable conformation of 2,3-dimethylbutane ?



31. Which of the following is the **best** example of torsional strain?

- A** the 60° bond angle in cyclopropane
B the 1,3-diaxial interaction in 1,1-dimethylcyclohexane
C the flagpole interaction in the boat conformation of cyclohexane
D the alignment of the C-H bonds in cyclopropane
E the strain in cyclopropane compared to cyclohexane

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

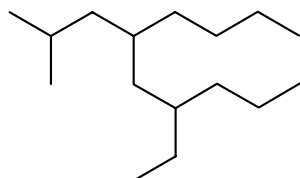
- A** chair > boat > twist boat
B chair > twist boat > boat
C boat > twist boat > chair
D boat > chair > twist boat
E twist boat > boat > chair

14% **PART 5: NOMENCLATURE**

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

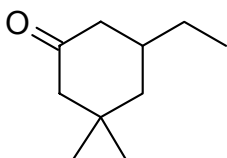
For each of questions 31 to 34, select the correct name for the compound shown:

33



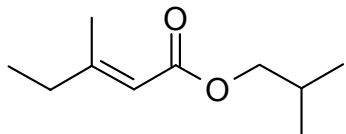
- A. 4-(2-ethylpentyl)-2-methyloctane
- B. 2-methyl-4-(2-ethylpentyl)octane
- C. 4-ethyl-6-(2-methylpropyl)decane
- D. 4-butyl-6-ethyl-2-methylnonane
- E. 4-ethyl-6-(1-methylpropyl)decane

34



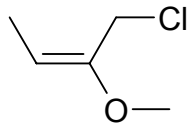
- A. 5-ethyl-3,3-dimethylhexanone
- B. 3-ethyl-5,5-dimethylcyclohexanone
- C. 5-ethyl-3,3-dimethylcyclohexanone
- D. 3,3-dimethyl-5-ethylcyclohexanone
- E. 5-ethyl-3,3-dimethylcyclohexanal

35



- A. n-butyl (E)-2-propenoate
- B. isobutyl (Z)-2-propenoate
- C. isobutyl (E)-3-methyl-2-pentenoate
- D. t-butyl methyl pentenoate
- E. butyl 3-methylpentyl ether

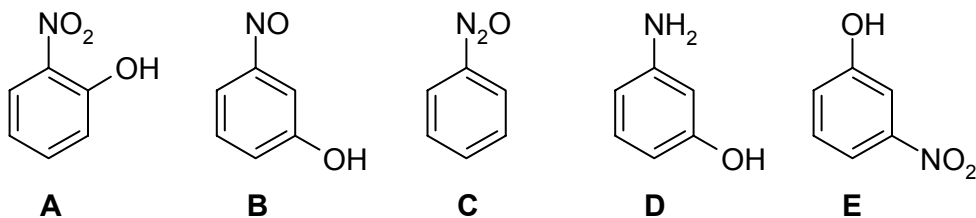
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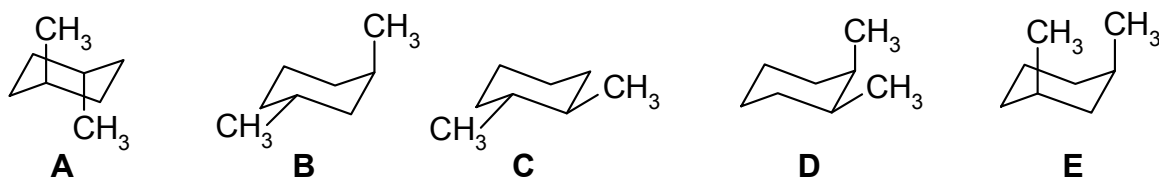
- A. (Z)-1-chloro-2-methoxybutane
- B. 3-chloro-2-hydroxypropene
- C. (Z)-1-chloro-2-methoxy-2-butene
- D. (Z)-4-chloro-3-hydroxy-2-butene
- E. (E)-1-chloro-2-methoxy-2-butene

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

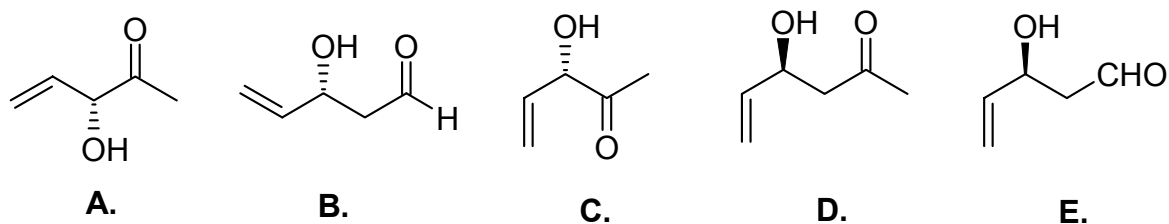
37. *meta*-nitrophenol



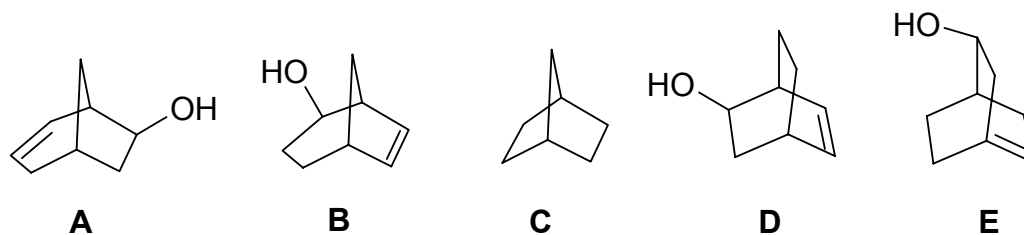
38. *trans* 1,2-dimethylcyclohexane :



39. (*S*)-3-hydroxy-4-penten-2-one :



40. 2-hydroxybicyclo[3.2.1]oct-6-ene:



12% 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 at a crash site involving a truck carrying the drum. The sample was determined to be a single compound by gas chromatography and elemental analysis indicated that the sample contained 62.04% C, 27.55% O and 10.41% H by weight.

- (a) Determine the molecular formula (which equals the empirical formula)
- (b) What is the IHD of this molecular formula? (IHD = index of hydrogen deficiency)
- (c) list **four** different functional groups that may be found in compounds with this formula
- (d) draw a pair of constitutional isomers and give their complete IUPAC names
- (e) draw a pair of enantiomers and assign their absolute configurations at the chiral centres.

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 which an alkyl halide, 3-bromo-1,4-pentadiene, is hydrolyzed in water to give two alcohols, 1,4-pentadien-3-ol and 2,4-pentadien-1-ol.

Step 1. Loss of a bromide ion from 3-bromo-1,4-pentadiene creating a resonance stabilized carbocation.

Step 2. Attack of a molecule of water (as a nucleophile) on the electrophilic carbon, leading to the formation an oxonium ion.

Step 3. An acid – base reaction in which a water molecule acting as a base removes a proton from the oxonium ion, producing the alcohol 1,4-pentadien-3-ol.

(b) Draw the major resonance contributors for the carbocation produced in step 1.

(c) Show, using curly arrows, how 2,4-pentadien-1-ol is formed from the carbocation drawn in **(b)**

(d) What type of isomers are 1,4-pentadien-3-ol and 2,4-pentadien-1-ol ?

12% **PART 8: THERMODYNAMICS**

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

There are four configurational isomers of 1-methyl-2-phenylcyclohexane.

Isomer **I** has a heat of combustion, ΔH_C° of -1733.15 kcal/mol.

The heats of formation, ΔH_f° , for the other 3 isomers are :

II = -13.53 kcal/mol, **III** = -11.45 kcal/mol, and **IV** = -9.49 kcal/mol

- (a) Given that the heats of combustion for graphite, ΔH_C° , C (graphite) = -94.05 kcal/mol and for hydrogen, ΔH_C° H₂ (gas) = -57.8 kcal/mol, calculate ΔH_f° , for isomer **I**
- (b) Draw the four configurational isomers of 1-methyl-2-phenylcyclohexane and :
- (i) match them to their corresponding ΔH_f° values
 - (ii) indicate whether they are *cis* or *trans* isomers
 - (iii) identify the most stable *cis* isomer and the most stable *trans* isomer
- (c) Use the principles of conformational analysis to explain your choices in (b) part iii

**** THE END ****