

THE UNIVERSITY OF CALGARY
FACULTY OF CONTINUING EDUCATION
FINAL EXAMINATION
CHEMISTRY 351

JUNE 28th 1999

Time: 3 Hours

READ ALL THE INSTRUCTIONS CAREFULLY

PLEASE WRITE YOUR NAME, STUDENT I.D. NUMBER ON **BOTH** YOUR EXAM 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. Parts 1 - 5 will be computer graded, and only Parts 6, 7, and 8 are to be answered on the paper provided. A periodic table with atomic numbers and atomic weights, and tables of NMR spectroscopic data are appended to the exam.

Parts 1 - 5 consist of a series of multiple choice questions numbered 1 - 49 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**.

20 PART 1 RELATIVE PROPERTIES

ANSWER ANY TEN (10) of Questions 1-14.

Arrange the items in Questions 1-14 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**

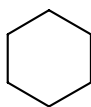
C. **ii > i > iii**

D. **ii > iii > i**

E. **iii > i > ii**

AB. **iii > ii > I**

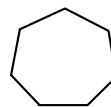
1. The relative ring strain per $-\text{CH}_2-$ in the following cycloalkanes:



i



ii



iii

2. The solubility in hexane of the following:

benzene

i

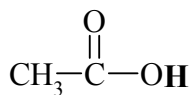
phenol

ii

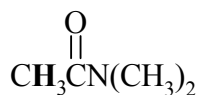
methoxybenzene

iii

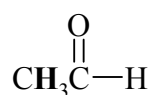
3. The relative acidity of the bold H in:



i

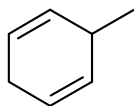


ii

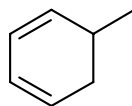


iii

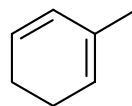
4. The heat of formation of the following alkenes (most endothermic to most exothermic):



i



ii

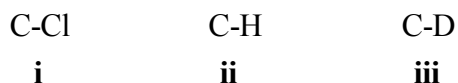


iii

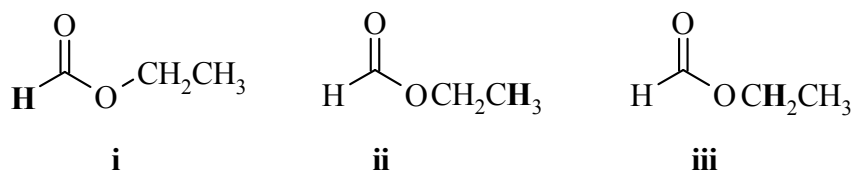
Use the following code to indicate your answers.

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

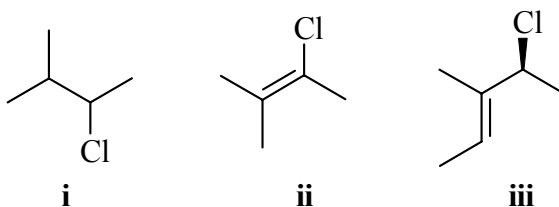
5. The typical IR stretching frequency of the following types of bonds:



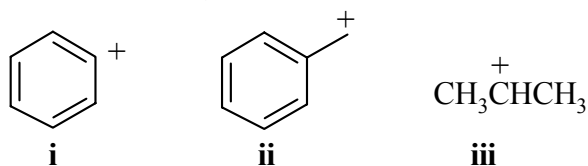
6. The relative ¹H nmr chemical shifts (δ / ppm) of the bold H in:



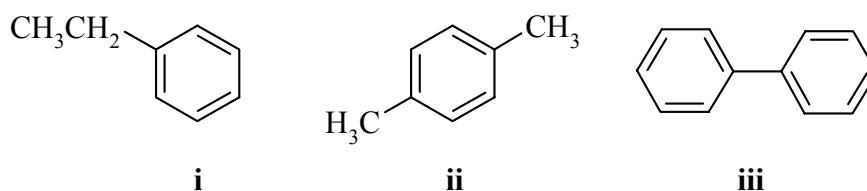
7. The number of stereoisomers of:



8. The stability of the following carbocations:



9. The number of different ¹³C nmr chemical shifts expected for the following molecules:



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**

10. The oxidation state of the carbon atoms in bold, **C**, in:



i

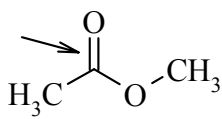


ii

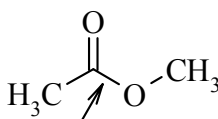


iii

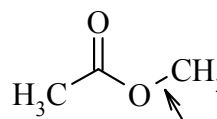
11. The IR stretching frequency in cm^{-1} of the indicated CO bond in:



i



ii



iii

12. The relative acidity of the following carboxylic acids:



i

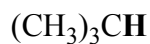


ii



iii

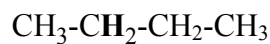
13. The multiplicity of the signals in the ^1H nmr spectra for the bold **H** in:



i

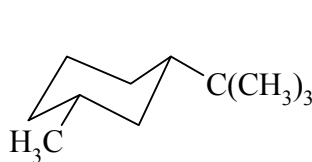


ii

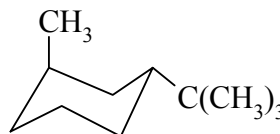


iii

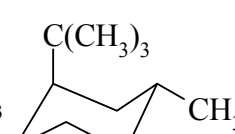
14. The relative energies of the following substituted cyclohexanes:



i



ii



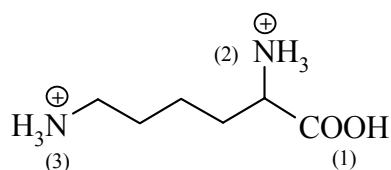
iii

12 PART 2 ACIDS AND BASES

ANSWER ALL of questions 15-22.

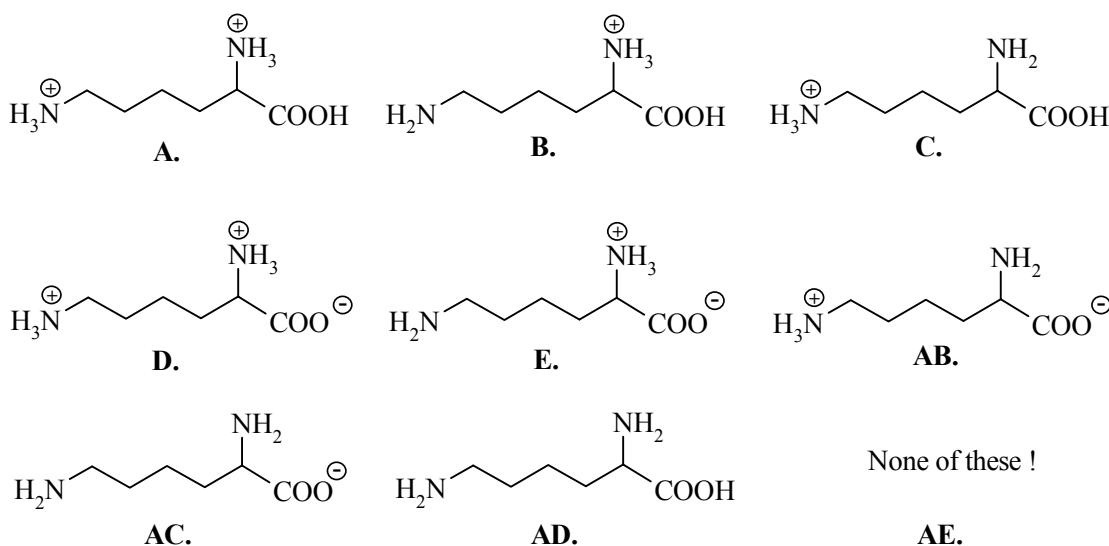
Shown below is the structure of the amino acid Lysine, and the pK_A 's of the acidic sites (1-3).

Select your answer for questions **15-18** from the options **A** to **AE** provided.



pK_A 1	2.18
pK_A 2	8.95
pK_A 3	10.53

Lysine



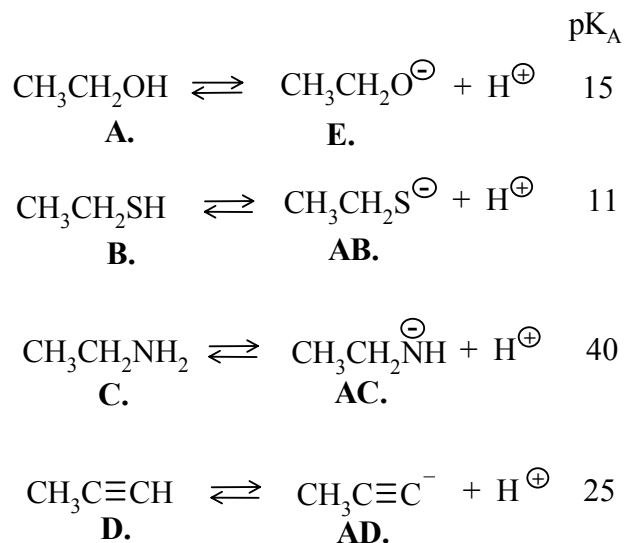
15. At $pH=3.0$, the predominant form of Lysine is?

16. At $pH=7.0$, the predominant form of Lysine is?

17. At $pH=11$, the predominant form of Lysine is?

18. Which species are electronically neutral AND can be observed experimentally ?

Answer questions 19 to 22 based on the following data for the series compounds.



Henderson-Hasselbach equation: $pK_A = \text{pH} + \log \frac{[\text{HA}]}{[\text{A}^-]}$

19. Which species is the strongest base ?

20. At pH = 9, what is the relative ratio of **B** to **AB** ?
 A. 1:100 B. 1:10 C. 1:1 D. 10:1 E. 100:1

21. Which species could protonate **E** ?

22. Consider an reaction of a 1:1 mixture of **B** and **E** as starting materials, then the resultant equilibrium would:
 A. Lie towards starting materials **B** and **E** with $K < 0.01$
 B. Lie towards starting materials **B** and **E** with $1 > K > 0.01$
 C. Be a balanced equilibrium where $K = 1$
 D. Lie towards the products **A** and **AB** with $100 > K > 1$
 E. Lie towards the products **A** and **AB** with $K > 100$

10 PART 3 LABORATORY

ANSWER ANY TEN (10) of questions 23 to 34.

For questions 23-34, decide whether the whole statement is true or false. If it is true, blacken A. If it is false, then blacken B. (1 Mark each question.)

23. Raoult's Law can be used explain the principles behind fraction distillation.

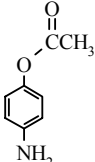
24. The ratio of the quantities of solute dissolved / ml in immiscible solvents is the partition (or distribution) coefficient.

25. Lactose is a carbohydrate.

26. Casein is an amino acid.

27. In order to be effective, recrystallisation requires that the compounds have different solubilities in the recrystallisation solvent.

28. A simple filtration should be carried out using a ceramic Buchner funnel.

29. The structure of Acetaminophen is 

30. In thin layer chromatography, if two compounds have the same R_f values, then they must be identical.

31. In the steam distillation of the natural product, the trap was used to make sure that the contents of the distillation flask are not sucked back into the steam line if the pressure of the steam line dropped.

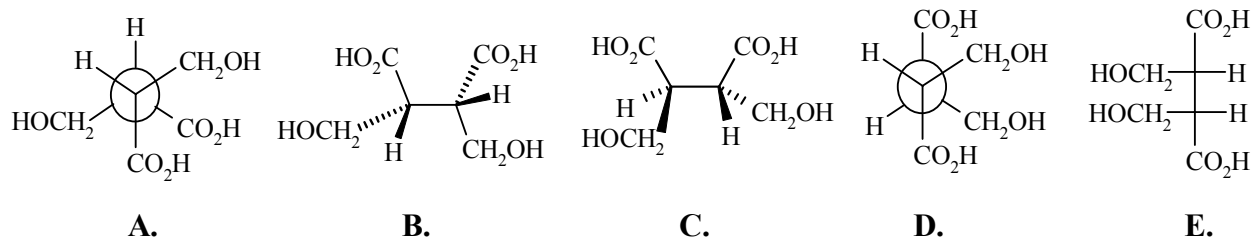
32. In an extraction using a separatory funnel, the organic phase will always be the top layer.

33. Fractional distillation can usually be used to separate mixtures of liquids if the components have reasonably different boiling points.

34. In order to determine the theoretical yield of a product, you need to divide the number of moles of the limiting reagent used by the number of moles of product obtained.

16 PART 4 STEREOCHEMISTRY

ANSWER ALL EIGHT (8) of the questions 35 to 42.



35. Choose any **TWO** compounds that are conformational isomers.
36. Choose any **TWO** compounds that are enantiomers.
37. Choose any **TWO** compounds that are diastereomers.
38. Choose **ALL** the compounds that are meso.
39. Choose **ALL** the compounds where the carboxylic acid groups are *gauche* to each other.

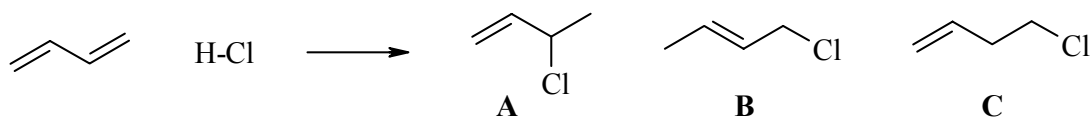
The specific rotation of (S,S) stereoisomer is $+25.0^\circ$. The optical rotation of a solution made up from 5g of a mixture stereoisomers **A** and **C** in 20 ml of water was measured in a 10cm cell. The observed rotation was -5.0° .

40. What is the specific rotation of the mixture ?
A. $+40.0^\circ$ B. $+20.0^\circ$ C. $+10.0^\circ$ D. -10.0° E. -20.0°
41. What is the relative ratio of **A** : **C** in the mixture ?
A. 90 : 10 B. 80 : 20 C. 70 : 30 D. 60 : 40 E. 30 : 70
42. What is the specific rotation of a mixture of 1 g **A** and 4 g of **D** dissolved in 20ml of water ?
A. $+25.0^\circ$ B. $+15.0^\circ$ C. -5.0° D. -15.0° E. -25.0°

10 PART 5 KINETICS & THERMODYNAMICS

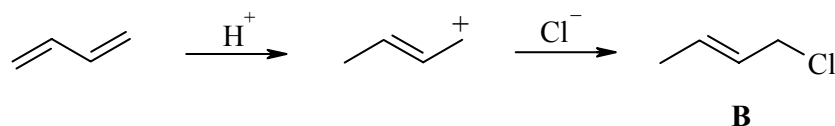
ANSWER ALL SEVEN (7) of the questions 43 to 49.

A student was studying the reaction of HCl with 1,3-butadiene and was considering various products:



Average Bond Energies / kcal mol ⁻¹	H-Cl	103	C=C	146
	H-C	99	C-C	83
	C-Cl	81	H-H	104

Experimentally the student found that a mixture of **A** and **B** was usually produced, but not product **C**. At low temperature (-20°C) **A** was the major product, but at higher temperatures (50°C) **B** was the major product. Initially the student calculated the heats of reaction for each of the products, but found them all to be the same. After looking in a textbook, the student discovered that the reaction proceeded via protonation of a C=C to give a carbocation intermediate, followed by attack of a chloride ion, as shown below for **B**:



Based on the information provided above, answer each of the following questions.

43. The calculated heat of reaction in kcal mol⁻¹ is:
 A. +85 B. +69 C. +14 D. -14 E. -85
44. Therefore these reactions are calculated to be: (1 mark)
 A. Exothermic B. Thermoneutral C. Endothermic
45. The carbocation that leads to product **C** would be:

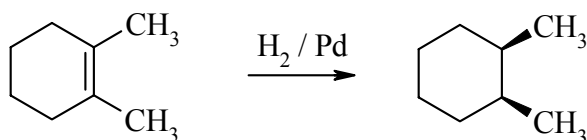
 A. B. C. D. E.

46. The reason why the carbocation that leads to **C** is NOT formed is:
- A. It is too sterically hindered
 - B. It is primary and is too unstable
 - C. It is primary, but is resonance stabilised
 - D. It is vinylic and is too unstable
 - E. None of these reasons.
47. The reason why the carbocation that leads to **B** is formed is:
- A. It is not sterically hindered
 - B. It is primary and is therefore stable
 - C. It is primary, but it is also resonance stabilised
 - D. It is vinylic and is unstable
 - E. None of these reasons.
48. Since product **A** is formed the most rapidly at low temperature it is:
- A. The thermal product
 - B. The kinetic product
 - C. The thermodynamic product
 - D. The substitution product
 - E. None of these
49. Product **B** is the thermodynamic product because:
- A. It is formed most rapidly
 - B. It is derived from a stable intermediate
 - C. The alkene in **B** is more stable than that in **A** or **C**
 - D. It has more C-H bonds than either **A** or **C**
 - E. None of these reasons

10 PART 6 MECHANISM

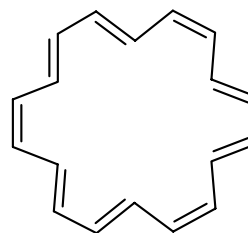
Answer **BOTH** parts. Write your answer in the booklet provided. Show your working as **PARTIAL** marks will be given.

- (a) Discuss the stereochemistry of the following experimental observations for the hydrogenation of a cyclic alkene. Is the observed stereochemistry of the product consistent with a carbocation intermediate? Explain.



- (b) The structure of an unusual hydrocarbon and its ¹H-nmr chemical shifts are shown below. Discuss the aromaticity of this compound, and by comparing with the typical ¹H-nmr chemical shifts observed for benzene and alkenes, suggest a reason for the observed chemical shifts. Note that the ¹³C-nmr only contains a single peak.

18-annulene
δ / ppm 8.8 and -1.9, integrating 2:1



10 PART 7 SPECTROSCOPY

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

The I.R., M.S., U.V., ^{13}C , and ^1H NMR spectral data of an unknown compound is provided. Determine the structure of this unknown compound.

DIAGRAMS WILL BE ADDED AS SOON AS TIME ALLOWS

IN THE ORIGINAL EXAM THEY WERE PHOTOCOPIED IN TO PLACE

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10 PART 8 STRUCTURE DETERMINATION

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

An unknown, but stable compound **A** (71.43 %C, 9.52 %H) was found to be chiral with an R configuration. The IR spectra showed absorptions at 3500cm^{-1} (strong, broad) and 1610cm^{-1} (medium). Hydrogenation of **A** using H_2 / Pd consumed only 1 mole equivalent of H_2 and gave a new compound **B** that was found to be achiral, and had a similar IR absorption at 3500cm^{-1} . Oxidation of **A** gave another achiral compound, **C** (73.17 %C, 7.32 %H), that lacked the IR absorption at 3500cm^{-1} but had an absorption at 1715cm^{-1} (strong). Hydrogenation of **C** using H_2 / Pd also consumed only 1 mole equivalent of H_2 and gave another new compound **D** that was also achiral, and had an IR absorption at 1745cm^{-1} (strong).

What are the structures **A – D** ?

Draw a wedge-hash diagram that shows the configuration of **A**.

THE END