THE UNIVERSITY OF CALGARY

FACULTY OF SCIENCE

MIDTERM EXAMINATION

CHEMISTRY 351

OCTOBER 30th 2002 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**

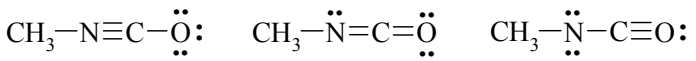
1. The C-C-C bond angle in each of the following molecules:

cyclopropane	propyne	propene
i	**ii**	**iii**

2. The number of constitutional isomers for each of the following molecular formulae:

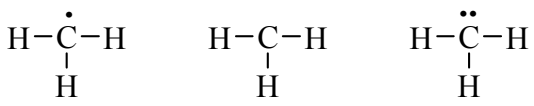
$C_4H_{10}O$	C_5H_{12}	C_3H_6
i	**ii**	**iii**

3. The relative importance of the following resonance contributors to CH_3NCO (no formal charges have been shown, but all required non-bonding or lone pair electrons are shown) :



i **ii** **iii**

4. The actual net or formal charge on the **carbon** atom in each of the following molecules (all required non-bonding or lone pair electrons are shown) :



i **ii** **iii**

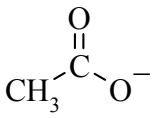
5. The relative acidity of the hydrogen atoms in each of the following hydrocarbons :

ethane	ethene	ethyne
i	**ii**	**iii**

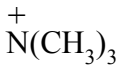
Use the following code to indicate your answers.

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

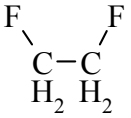
6. The total number of valence electrons in each of the following molecules or ions (no lone pairs or non-bonding electrons are shown) :



i

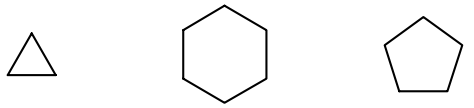


ii



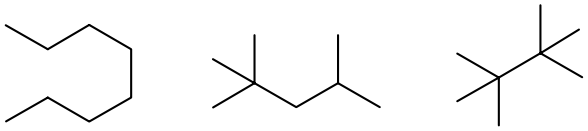
iii

7. The heat of formation, ΔH_f^o, per methylene (-CH_2-) in each of the following molecules: (least exothermic to most exothermic)



i **ii** **iii**

8. The boiling point of each of the following isomeric hydrocarbons :

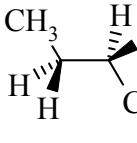


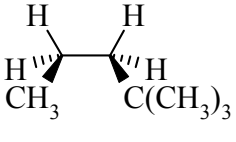
i **ii** **iii**

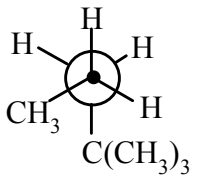
9. The relative energies of the photons of the following wavelength, wavenumber or frequency (Planck's constant, h = 6.63 x 10-^{34} Js, c = 3 x 10^8 m/s) :

500 nm	1715 cm^{-1}	60 MHz
i	**ii**	**iii**

10. The relative energies of the following conformations of 2,2-dimethylpentane :







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 1g of solute in 50ml of water, what % of the solute will have been extracted after extraction and separation with 2 x 50ml portions of dichloromethane ?

    A 100 % **B** 75 % **C** 50 % **D** 25 % **E** 0 %

12. If a pure liquid sample has an observed boiling point in Calgary of 200 ^{o}C, then what would be the sea level corrected boiling point ?

    A 225 ^{o}C **B** 210 ^{o}C **C** 200 ^{o}C **D** 190 ^{o}C **E** 175 ^{o}C

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

    A heating the distillation flask more vigourously
    B heating the distillation flask more cautiously
    C use a longer fractionating column
    D use a shorter fractionating column
    E increasing the flow of cooling water in the fractionating column

14. Which of the following experimental methods would be most suitable for the purification of a solid contaminated with a small amount of a non-volatile impurity ?

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

15. How many types of hydrogen and carbon are there in 1,3-dimethylbenzene ?

A 2H, 2C **B** 3H, 4C **C** 3H, 3C **D** 4H, 4C **E** 4H, 5C **AB** 5H, 5C

16. Ferric chloride was used in the synthesis of aspirin for which of the following reasons :

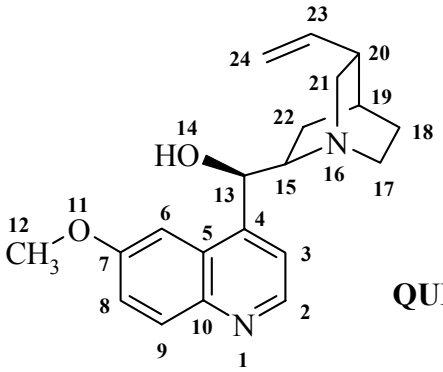
A to remove unreacted salicylic acid
B to remove the polymeric by-product
C to test for the presence of unreacted salicylic acid
D to confirm the structure of the aspirin
E to remove excess acetic anhydride

14% **PART 3: MOLECULAR PROPERTIES**

ANSWER ALL of the questions 17 - 23 (2 marks per question)

For each of the **questions 17 - 23** about QUININE (shown 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.



QUININE

17. What is the oxidation state of **C13**?

A. +2 **B**. +1 **C**. 0 **D**. -1 **E**. -2

18. Of the following list, which atom(s) is (are) sp^3 hydridised?

A. **N1** **B**. **C5** **C**. **O14** **D**. **N16** **E**. **C21**

19. Which of the following carbon atoms are tertiary ?

A. **C2** **B**. **C12** **C**. **C19** **D**. **C20** **E**. **C22**

20. Which carbon atom(s) is (are) *ortho* to a methoxy group ?

A. **C5** **B**. **C6** **C**. **C7** **D**. **C8** **E**. **C10**

21. Which of the following functional groups are found in QUININE ?

A. Alcohol **B**. Amide **C**. Ester **D**. Ether **E**. Phenol

22. How many units of unsaturation are there in QUININE ?
(units of unsaturation is the same as the index of hydrogen deficiency or IHD)

A. 7**B**. 8 **C**. 9 **D**. 10 **E**. 12

23. Which of the following **CC** bonds in QUININE is the shortest ?

A. **C8-C9** **B**. **C4-C13** **C**. **C13-C15** **D**. **C20-C23** **E**. **C23-C24**

12% **PART 4: CONFORMATIONAL ANALYSIS**

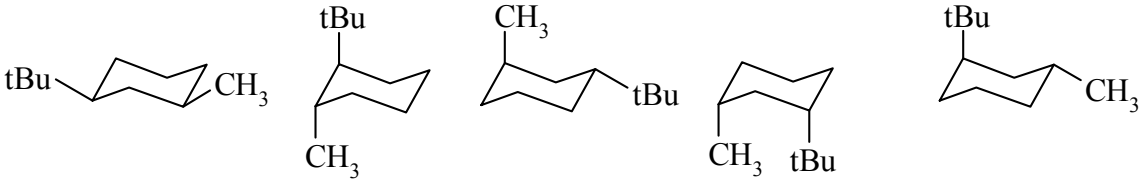
ANSWER ALL of the questions 24-29 (2 marks per question).

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

24. Which one of the following terms **best** describes a pair of structures with the same molecular formula, yet containing different functional groups ?

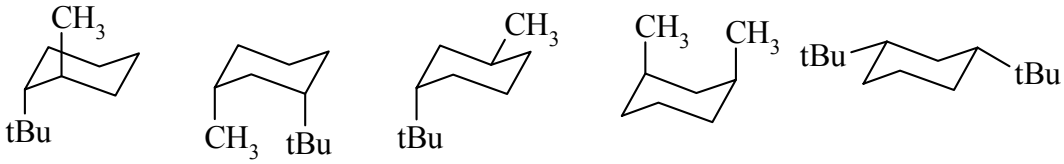
A cis-trans isomers **B** configurational isomers **C** diastereomers
D constitutional isomers **E** conformational isomers **AB** geometric isomers

25. Which of the following best represents the **most** stable conformation of *trans*-1-t-butyl-3-methylcyclohexane ?



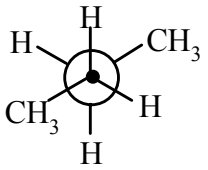
A **B** **C** **D** **E**

26. Which of the following molecules **in the conformations shown** has the worst single 1,3-diaxial interactions ?



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

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

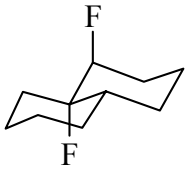


A anti **B** syn **C** gauche **D** eclipsed
E cis **AB** trans

28. In a chair conformation of cyclohexane there are two distinct types of hydrogens, axial and equatorial. How many types of hydrogen are there in the boat form ?

A. 2 **B**. 3 **C**. 4 **D**. 5 **E**. 6 **AB**. 12

29. How many axial hydrogens are there in the following compound in the conformation shown ?

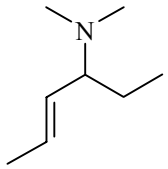


A 6 **B** 7 **C** 8 **D** 9 **E** 10 **AB** 12

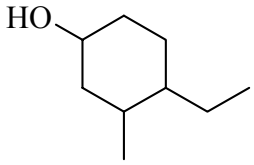
14% **PART 5: NOMENCLATURE**

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

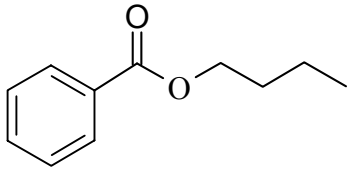
For each of questions 30 to 34, select the correct name for the compound shown:

30. 

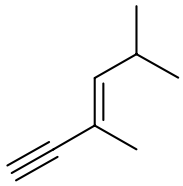
A. (E)-4-amino-2-hexene
B. (Z)- 4-amino-2-hexene
C. (E)-N,N,1-trimethyl-3-amino-1-pentene
D. (Z)-N,N-dimethyl-2-hexenamide
E. (E)-4-(N,N-dimethylamino)-2-hexene

31. 

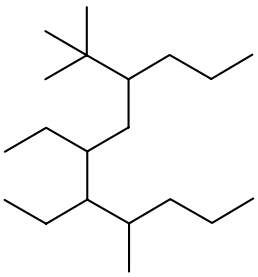
A. 4-ethyl-3-methylphenol
B. 4-ethyl-5-methylphenol
C. 4-ethyl-3-methylcyclohexanol
D. 3-methyl-4-ethylcyclohexanol
E. 4-ethyl-3-methylhexanol

32. 

A. benzyl n-butyl ether
B. n-butyl benzoate
C. n-butyl phenyl ether
D. phenyl butanoate
E. isobutyl benzoate

33. 

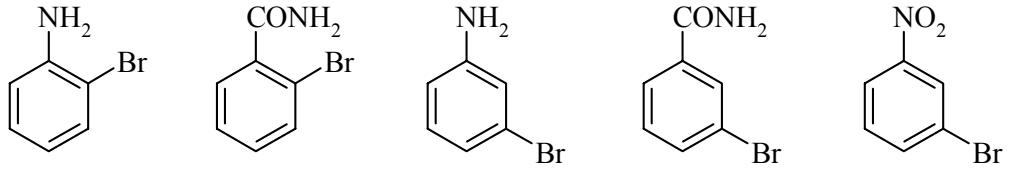
A. (E)-3,5-dimethylhex-3-en-1-yne
B. (Z)-3,5-dimethylhex-3-en-1-yne
C. (E)-2,4-dimethylhex-3-en-5-yne
D. (E)-3,5-dimethylhex-1-yn-3-ene
E. (Z)-2-ethynl-4-methylpent-2-ene

34. 

A. 6-*tert*-butyl-4-ethyl-3-*sec*-pentylnonane
B. 8-(1,1-dimethylethyl)-5,6-diethyl-4-methylundecane
C. 4-*tert*-butyl-6,7-diethyl-8-methylundecane
D. 5,6-diethyl-8-(1,1-dimethylethyl)-4-methylundecane
E. 4-methyl-5,6-diethyl-8- *tert*-butyl-undecane

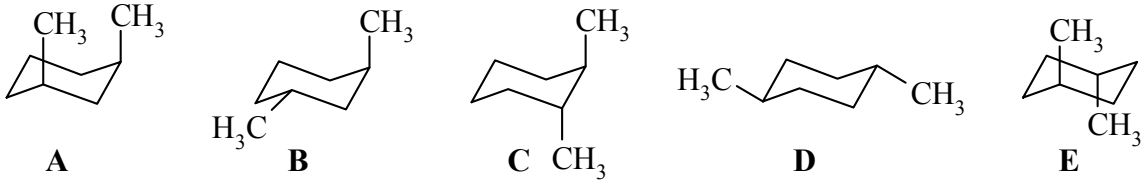
For each of questions 35 to 38, select the correct structure for the name provided:

35. *meta*-bromobenzamide



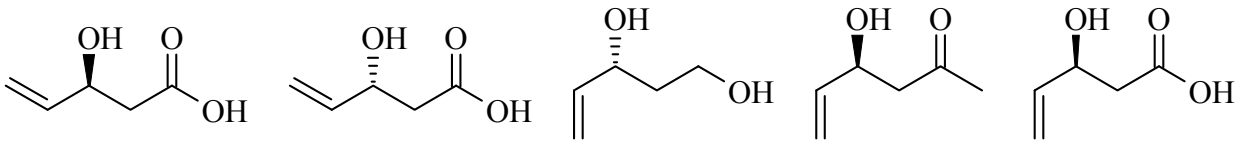
A **B** **C** **D** **E**

36. *trans* 1,3-dimethylcyclohexane :



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

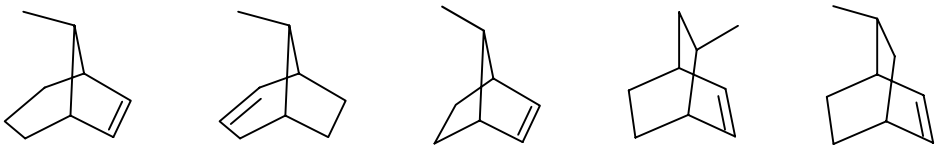
37. (R)-3-hydroxy-4-pentenoic acid :



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

38. 8-methylbicyclo[3.2.1]oct-6-ene:

Value



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

Value

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 was performed on a sample taken from an unlabelled drum found buried in the ground in a former industrial area. The result indicated that the sample contained 85.63% C and 14.37% H by weight.

(a) Use the combustion analysis data to determine the empirical formula.

(b) If the sample contains 6 carbon atoms, what is the molecular formula ?

Using this molecular formula draw :

(c) a pair of enantiomers

(d) a pair of constitutional isomers

(e) a pair of geometric isomers

Value

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 a ketone, 2-propanone, undergoes alkylation to give a new ketone, 2-pentanone when reacted with a base then an alkylating agent.

Step 1. An acid - base reaction in which a proton is removed from the 2-propanone using a base, sodium t-butoxide, to create a resonance stabilised carbanion and t-butanol.

Step 2. Attack of the carbanion (as a nucleophile) on the electrophilic carbon of ethyl bromide leading to the formation of a new CC sigma bond and causing the simultaneous loss of a bromide ion.

Answer the following questions :

Draw the significant resonance contributors for :
(i) the starting material 2-propanone, and
(ii) the carbanion formed from 2-propanone

The pKa for the H atom removed in 2-propanone is about 20, yet in propane the pKa is over 50. Explain why there is such a large difference in acidity.

Based on the information provided in this question, what alkylating agent should you use if you wanted to prepare 2-decanone ?

Value

12% **PART 8: THERMODYNAMICS**

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

DATA

The heat of formation, ΔH_f^o for butane is -30.4 kcal/mol and 2-methylpropane is -32.4 kcal/mol.

Combustion of 6.37g of 2-methylpropane (as a gas) produced 75.2 kcal of heat (measured using a calorimeter).

QUESTIONS

A. Write out the balanced equation that defines the heat of formation of butane.

B. Write out the balanced equation for the complete combustion of 2-methylpropane.

C. Roughly sketch where butane and 2-methylpropane would be placed on an energy level diagram (energy on the y-axis) relative to the other species in the equations from part A and part B.

D. Using the above data, calculate the heat of combustion of butane (as a gas) on a per mole of butane basis (kcal/mol)

****THE END****