THE UNIVERSITY OF CALGARY

FACULTY OF SCIENCE

FIRST MIDTERM EXAMINATION

CHEMISTRY 351

OCTOBER 29th 1997. Time: 2 Hours

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

Read the instructions carefully. 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 end of the exam.

Parts 1 - 5 consist of a series of multiple choice questions numbered 1 - 41 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***.

Value

14 PART 1 RELATIVE PROPERTIES

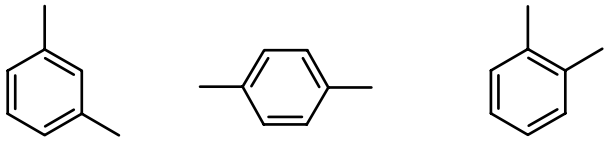
ANSWER ANY SEVEN (7) of Questions 1-8**.**

Arrange the items in Questions 1-8 in **DECREASING ORDER** (i.e. greatest, most etc. first) with respect to the indicated property.

Use the following code to indicate your answers.

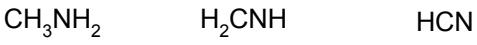
A.	i > ii > iii	D.	ii > iii > i
B.	i > iii > ii	E.	iii > i> ii
C.	ii > i > iii	AB.	iii > ii > i

1. The number of types of H in the following molecule:



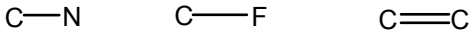
i **ii** **iii**

2. The H-C-N bond angle in each of the following:



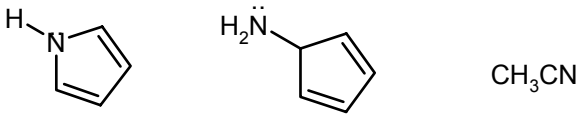
i **ii** **iii**

3. The polarity of the following bonds:



i **ii** **iii**

4. The C-N bond lengths in:



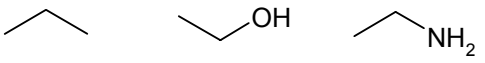
i **ii** **iii**

Value

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 relative boiling points:



i **ii** **iii**

6. The molecular dipole moments of:

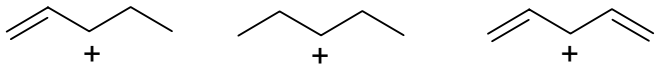
CH_3Cl $CHCl_3$ CO_2

i **ii** **iii**

7. The basicity (or availability) of the indicated lone pair in each of the following molecules:

i **ii** **iii**

8. The relative carbocation stability:



i **ii** **iii**

Value

13 PART 2: LABORATORY

ANSWER ALL of the questions 9-18.

For questions 9-15, 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)

9. When performing an extraction, it is better to use 2 x 50 ml portions rather than a single 100 ml portion of the extracting solvent to maximize the yield.

10. In thin layer chromatography, separation is obtained by partitioning a sample between a stationary phase and a mobile phase.

11. Traces of water in an organic solvent can be removed by adding anhydrous magnesium sulphate.

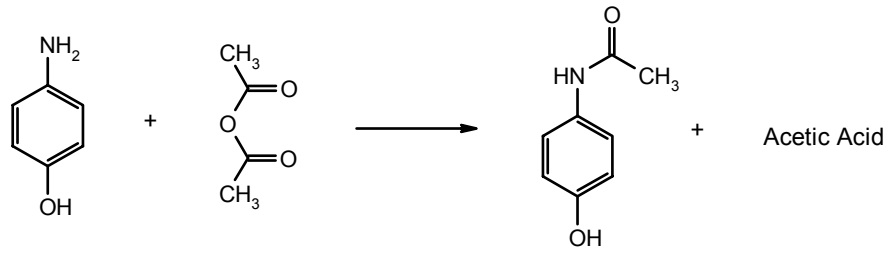
12. Sodium sulphate can be added to organic solutions to absorb coloured impurities and then be removed by filtration to purify contaminated materials.

13. In chromatography, if 2 compounds have the same Rf value, then they must be identical.

14. When carrying out a fractional distillation it is important to heat the distilling flask vigorously to ensure that equilibrium between the solution and the vapour is rapidly obtained.

15. When recording the boiling point of a liquid it is important to correct to the sea level value for literature comparisons since boiling point decreases with increasing pressure.

Questions **16-18** (2 marks per question) refer to the following reaction scheme:



	Aminophenol	Acetic anhydride	Acetaminophen
MW	109	102	151
Density		1.08g/ml	

A student used 1.09g of aminophenol and 1.25ml of acetic anhydride, and obtained 1.1g of crude acetaminophen, and 0.75g of pure material after recrystallisation.

Note 1 mmol = 0.001 mol

16. How many moles of the limiting reagent were used ?

A. 10 mmol B. 10.6 mmol C. 12.25 mmol D. 100 mmol E. 1 mmol

17. What was the % yield of crude acetaminophen ?

A. < 60% B. 60-70% C. 70-80% D. 80-90% E. >90%

18. How many mmoles of pure acetaminophen were obtained ?

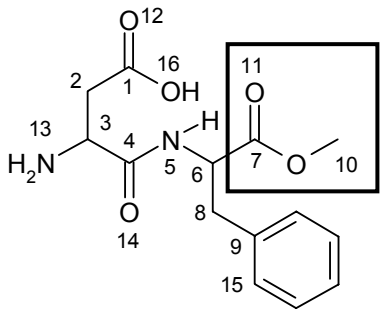
A. 50 B. 7.3 C. 5.0 D. 0.73 E. 0.50

Value

14 PART 3: MOLECULAR PROPERTIES

ANSWER ALL of the questions 19 - 25.

For each of the questions 19 - 25 about ASPARTAMINE (below), select the answer from those provided:



ASPARTAMINE
(Nutrasweet)

19. What is the oxidation state of C7?

A. +3 B. +2 C. 0 D. -2 E. -3

20. What is the oxidation state of C4?

A. +3 B. +2 C. 0 D. -2 E. -3

21. Which bond is the shortest bond:

A. C2-C3 B. C8-C9 C. C9-C15 D. C6-C7

22. The functional group in the box is a:

A. Carboxylic acid B. Aldehyde C. Ketone D. Methyl ester E. Methyl ether

23. Which of the following carbonyl C atoms has the *smallest* partial positive charge:

A. C1 B. C4 C. C7

24. What is the index of hydrogen deficency (IHD) of Aspartamine ?

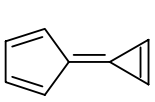
A. 5 B. 6 C. 7 D. 7.5 E. 8

25. Which of the following atoms is most basic ?

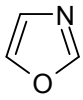
A. N13 B. N5 C. O14 D. C9 E. O16

14 PART 4: AROMATICITY AND RESONANCE

ANSWER ANY SEVEN (7) of the questions 26-33.

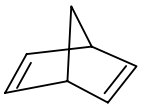


A

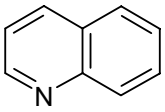


B

C

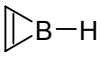


D



E

AB



AC

AD

AE

BC

For each of the questions 26-33 select a compound from the list above that is **best** described as:

26. A 6π, aromatic system.

27. A 4π, anti-aromatic system.

28. A 10π, aromatic system.

29. A 2π, aromatic system.

30. Non-aromatic as drawn, but has an aromatic conjugate base.

31. Non-aromatic as drawn, but has an important resonance structure that is aromatic.

32. A non-conjugated hydrocarbon.

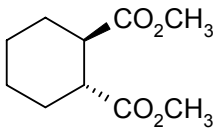
33. Non-aromatic as drawn, but on loss of a hydride gives an aromatic cation.

14 PART 5: NOMENCLATURE

ANSWER ANY SEVEN (7) of the questions 34-41.

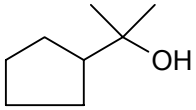
For each of questions 34 to 41, select the correct name for the compound shown:

34.



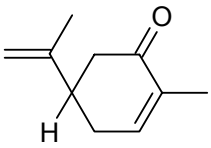
A. Dimethyl *cis*-1,2-cyclohexanedicarboxylate
B. Dimethyl *trans*-1,2-cyclohexanedicarboxylate
C. *trans*-1,2-dimethylcyclohexane
D. *cis*-1,2-dimethylcyclohexane
E. Methyl *trans*-1,2-cyclohexanecarboxylate

35.



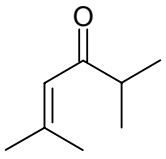
A. 1-cyclopropyl-1-methylethanol
B. 1-cyclopentyl-1-methylethanol
C. 1-cyclopentyl-1-methylethanal
D. 2-cyclopentyl-2-methylethanol
E. 1-cyclopentylisopropanol

36.



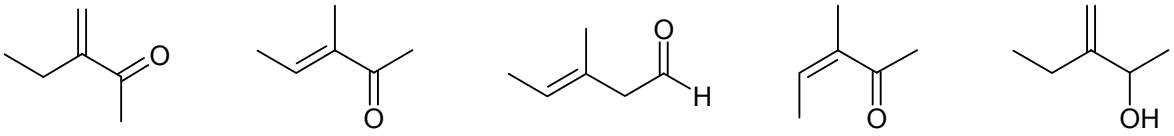
A. 5-Methyl-3-(1-methylethenyl)-4-cyclohexenone
B. 2-Methyl-5-(2-methylethenyl)-2-cyclohexenone
C. 2-Methyl-5-(1-ethylmethenyl)-2-cyclohexenone
D. 2-Methyl-5-(1-methylethenyl)-2-cyclohexenone
E. 2-Methyl-5-(1-methylethenyl)cyclohexanone

37.



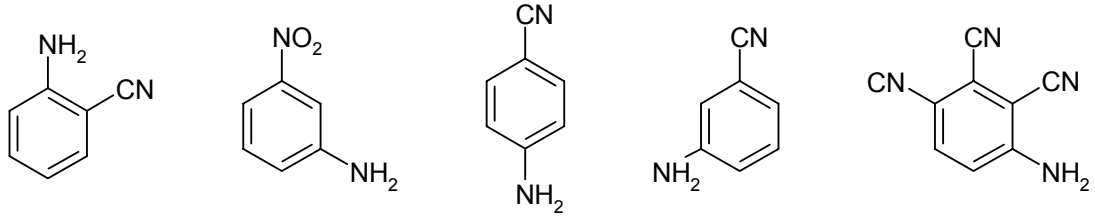
A. (Z)-2,5-dimethyl-4-hexene-3-one
B. (E)-2,5-dimethyl-4-hexene-3-one
C. (Z)-2,5-dimethyl-2-hexene-4-one
D. (E)-2,5-dimethyl-2-hexene-4-one
E. 2,5-dimethyl-4-hexene-3-one

38. (E)-3-methylpent-3-en-2-one



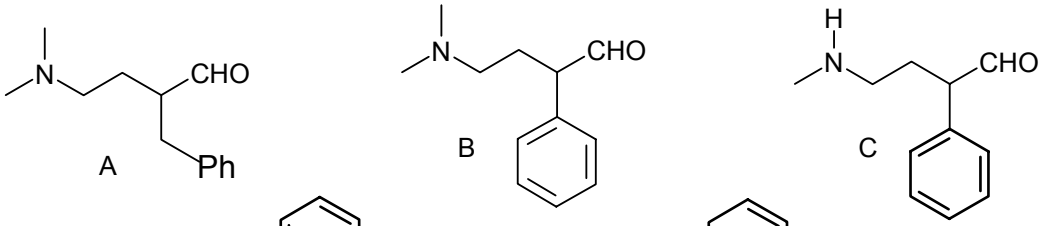
A B C D E

39. 3-Cyanoaniline:



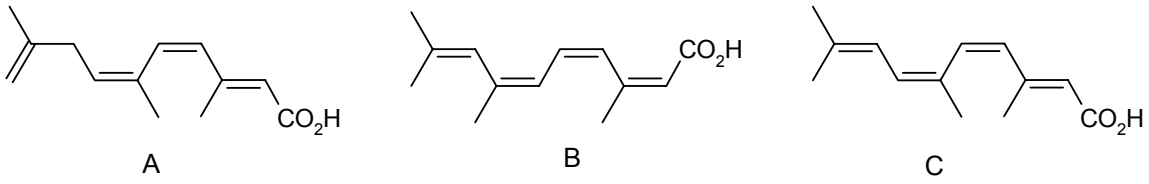
A B C D E

40. 2-Phenyl-4-(N,N-dimethylamino)butanal:



A B C D E

41. (2E,4Z,6Z)-3,6,9-trimethyl-2,4,6,8-decatetraenoic acid:



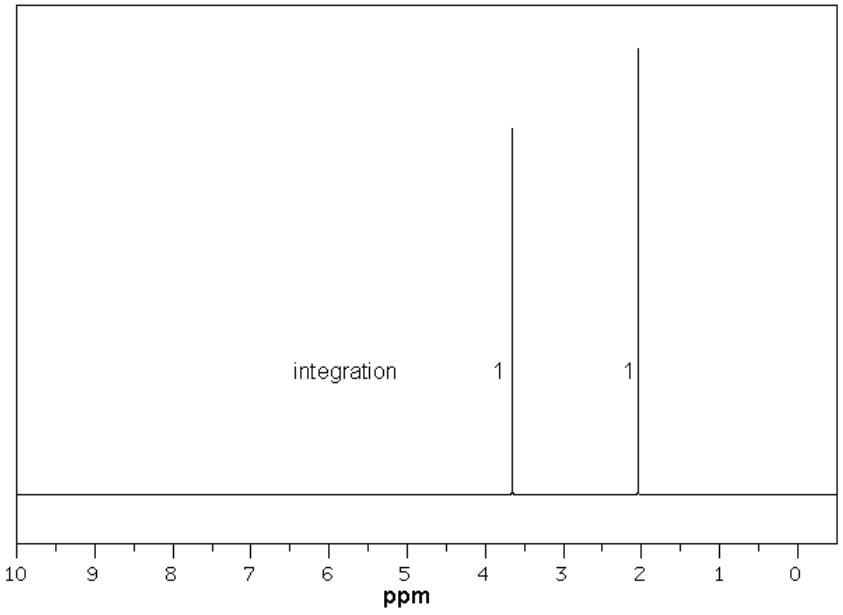
A B C D E

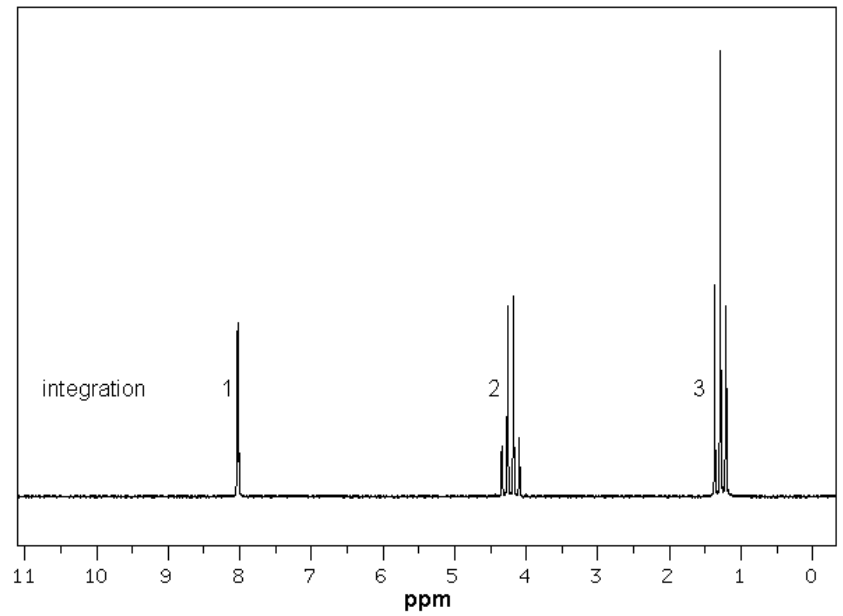
Value

10 PART 6: STRUCTURE DETERMINATION:

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

A combustion analysis was performed on a sample from a crime scene. The result indicated that the sample contained 48.6% C, 8.2% H, 43.2% O. The sample was injected into a gas chromatograph and two peaks were detected with very similar retention times. These two compounds were found to be isomers. Use the combustion analysis data to determine the empirical formula then use the ^{1}H NMR to determine the structure of the two isomers.





Value

11 PART 7: MECHANISM:

Write your answer in the booklet provided.

Draw a mechanism using double headed (ie electron pair) curly arrows that represents the reaction described by the following points.

1. Protonation of 1-phenylethanol by hydrochloric acid to give an oxonium ion.
2. Loss of water from this species to form a fairly stable carbocation.
3. Abstraction of a proton from the carbocation by a base to produce phenylethene (styrene)

Draw resonance structures to show the stability of the carbocation.

Value

10 PART 8: THERMODYNAMICS

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

Gasoline mainly consists of two isomers of octane, 2,2-dimethylhexane ΔH_c = -1304.6 kcal/mol and 2,2,3,3-tetramethylbutane ΔH_c = -1303.0 kcal/mol. Knowing that the heats of combustion, ΔH_c C (graphite) = -94.05 kcal/mol and ΔH_c H_2 (gas) = -57.8 kcal/mol, calculate the heat of formation, ΔH_f for each of the isomers of octane. Based on this data, which isomer is the most stable?

****THE END****