

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

JUNE 10th 1998.

Time: 2 Hours

READ THE INSTRUCTIONS CAREFULLY.

PLEASE WRITE YOUR NAME, STUDENT I.D. NUMBER ON **BOTH** YOUR EXAM 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 spectroscopic data are appended to the end of the exam.

Parts 1 - 5 consist of a series of multiple choice questions numbered 1 - 42 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**.

14 **PART 1 RELATIVE PROPERTIES**

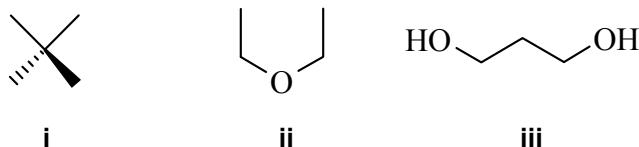
ANSWER ANY SEVEN (7) of Questions 1-8.

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

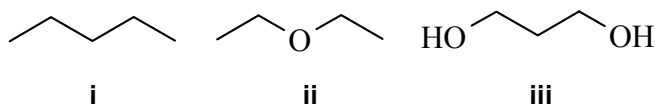
Use the following code to indicate your answers.

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

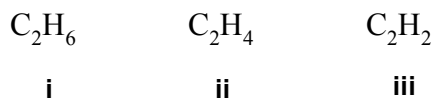
1. The relative boiling points of the following:



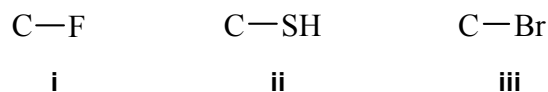
2. The solubility in hexane of the following:



3. The H-C-C bond angles in the following:



4. The IR stretching frequency (cm^{-1}) of the following carbon-heteroatom bond types:



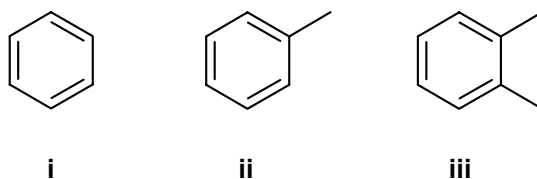
Use the following code to indicate your answers.

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

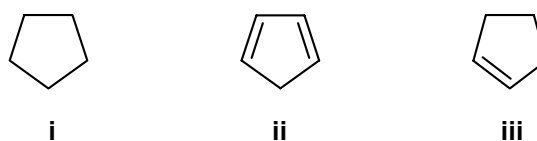
5. The heats of combustion of the following isomeric hydrocarbons:

- i n-octane
- ii 2,5-dimethylhexane
- iii 2,2,3,3-tetramethylbutane


6. The number of peaks in the proton decoupled ^{13}C NMR of the following:



7. The pKa of the most acidic H for each of the following molecules:



8. The multiplicity of the methylene group (-CH₂-) signals in the H NMR for each of the following:

- i $\text{CH}_3\text{CH}_2\text{CH}_3$
- ii $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$
- iii 

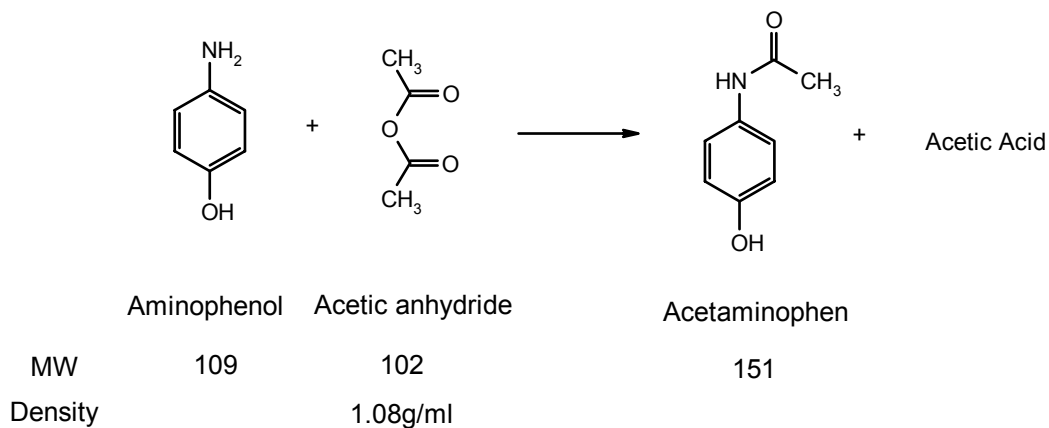
13 **PART 2: LABORATORY**

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, the organic solvent and the aqueous phase should be miscible.
10. In chromatography, separation is obtained by partitioning a sample solute between a stationary phase and a mobile phase.
11. When measuring a melting point, it is important to heat the sample strongly near the melting point to ensure that the crystals melt quickly to keep a narrow melting point range.
12. Activated charcoal can be added to organic solutions to absorb coloured impurities, and then be removed by filtration as a method of purification for contaminated materials.
13. Recrystallisation can be used to purify samples because small quantities of impurities remain in solution when the crystals of the sample form.
14. When carrying out a fractional distillation it is important to run water through the distillation column such that it flows in through the bottom and out at the top to ensure that the vapours condense.
15. When recording the boiling point of a liquid it is important to correct to the sea level value for literature comparisons since the boiling point of a liquid increases with decreasing pressure.

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



An organic chemistry student used 2.18g of aminophenol and 1.51ml of acetic anhydride, and obtained 2.0g of crude acetaminophen, and 1.51g of pure material after recrystallisation.

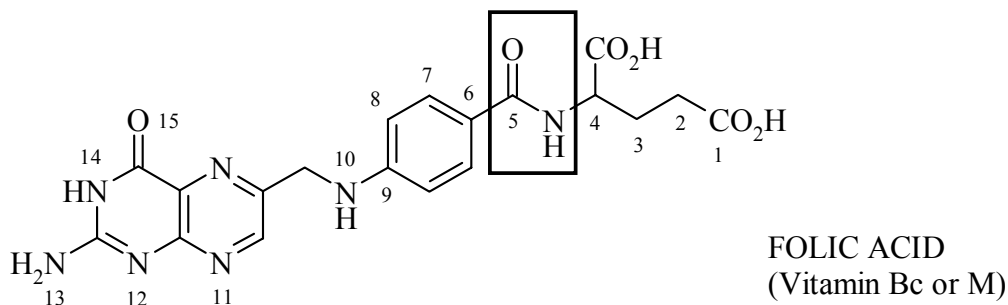
Note 1 mmol = 0.001 mol

16. How many moles of the limiting reagent were used ?
- A. 20.0 mmol B. 1.73 mmol C. 17.3 mmol D. 1.60 mmol E. 16 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. 0.01 B. 0.1 C. 1.0 D. 10 E. 100

14 **PART 3: MOLECULAR PROPERTIES**

ANSWER ALL of the questions 19 - 25.

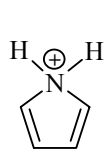
For each of the questions 19 - 25 about FOLIC ACID (Vitamin Bc or M) shown below, select the answer from those provided:



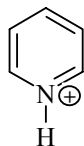
19. What is the oxidation state of C1?
A. +3 B. +2 C. 0 D. -2 E. -3
20. What is the stretching frequency (in cm^{-1}) of the C=O bond in the box ?
A. 1715 B. 1695 C. 1670 D. 1650 E. 1620
21. Which of the following bonds is the shortest:
A. C1-C2 B. C2-C3 C. C5-C6 D. C7-C8
22. The functional group in the box is an example of:
A. Carboxylic acid B. Amine C. Amide D. Aldehyde E. Ketone
23. Since N 14 is involved in resonance with the adjacent carbonyl what is the hybridisation of the N 14 ?:
A. Unhybridised B. sp^3 C. sp^2 D. sp E. sp^3d^2
24. What is the index of hydrogen deficiency (IHD) of Folic acid ?
A. 11 B. 11.5 C. 12 D. 13 E. 14
25. What is the approximate pKa of the carboxylic acid that includes C1 ?
A. -5 B. 0 C. 5 D. 10 E. 15

14 **PART 4: AROMATICITY AND RESONANCE**

ANSWER ANY SEVEN (7) of the questions 26 - 34.



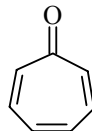
A.



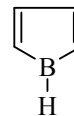
B.



C.



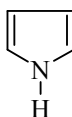
D.



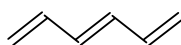
E.



AB.



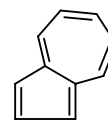
AC.



AD.



AE.



BC.

For each of the questions 26 - 34 select a compound from the list above that is **best** described as:

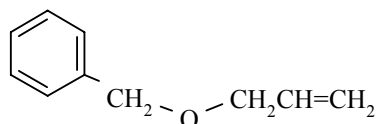
26. A 6π , aromatic system.
27. A 4π , anti-aromatic system.
28. A 10π , aromatic system.
29. A 2π , aromatic system.
30. A 6π , conjugated, non-aromatic system
31. Non-aromatic as drawn, but has an important resonance structure that is aromatic.
32. A non-conjugated hydrocarbon.
33. Non-aromatic as drawn, but on loss of a hydride gives an aromatic cation.
34. Non-aromatic as drawn, but has an aromatic conjugate base.

14 **PART 5: NOMENCLATURE**

ANSWER ANY SEVEN (7) of the questions 35-42.

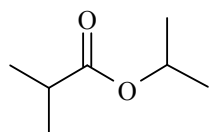
For each of questions 35 to 42, select the correct name for the compound shown:

35.



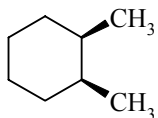
- A. Allyl phenyl ether
- B. Allyl benzyl ether
- C. Vinyl phenyl ether
- D. Benzyl vinyl ether
- E. 4-oxa-5-phenyl-1-pentene

36.



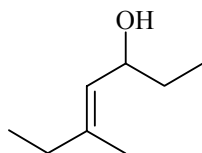
- A. Diisopropyl oxaketone
- B. Propyl 1-methylpropanoate
- C. 2-propyl propanoate
- D. 2-propyl 2-methylpropanoate
- E. Diisopropyl ester

37.



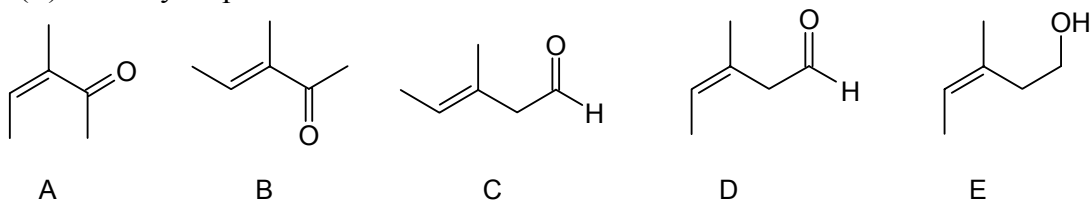
- A. Dimethylcyclohexene
- B. Dimethylcyclohexane
- C. *trans*-1,2-dimethylcyclohexane
- D. *cis*-1,2-dimethylcyclohexane
- E. 1,1-dimethylcyclohexane

38.

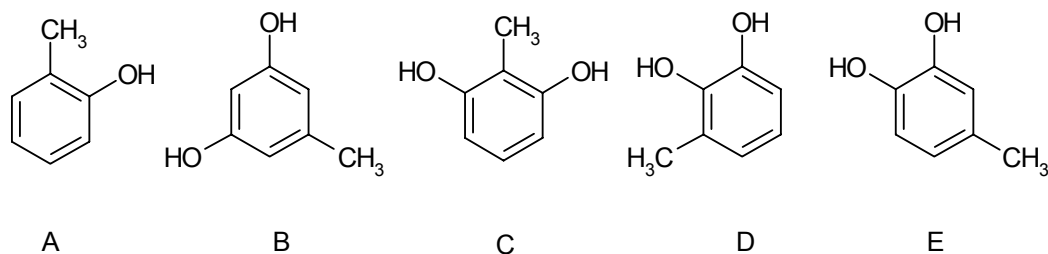


- A. (E)-5-methylheptan-3-al
- B. (Z)-3-methyl-3-hepten-5-al
- C. (E)-5-methyl-4-hepten-3-ol
- D. (Z)-5-methyl-4-hepten-3-ol
- E. 5-methyl-4-hepten-3-ol

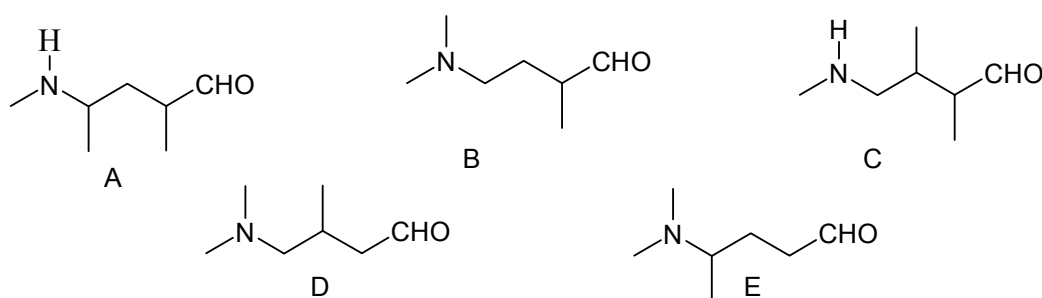
39. (Z)-3-methyl-3-pentenal



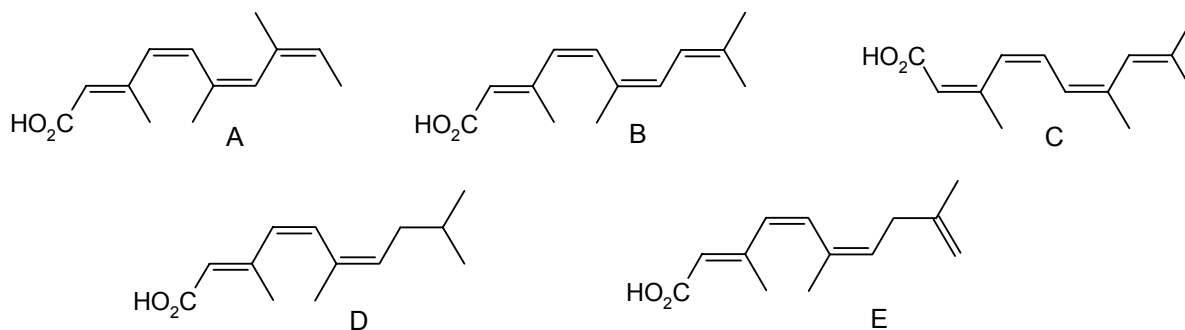
40. 2,6-dihydroxytoluene:



41. 4-(N,N-dimethylamino)-3-methylbutanal:



42. (2Z,4Z,6Z)-3,7,9-trimethyl-2,4,6,8-decatetraenoic acid:



10 **PART 6: STRUCTURE DETERMINATION:**

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

A sample of a liquid was obtained from the scene of a chemical spill involving a derailed tanker car. In the laboratory it was determined that the sample contained 54.30 % C, 5.57 % H (no analysis for other atoms was attempted). Spectroscopic analysis of the sample produced the IR, MS, UV, ^{13}C / ^1H NMR spectra shown below. Use the data provided to determine the structure of the spilled material.

11 **PART 7: MECHANISM:**

Write your answer in the booklet provided.

Draw a mechanism sequence using double headed (ie electron pair) curly arrows that represents the reaction sequence described verbally by the following points in which phenylethene is treated with aq. sulphuric acid to give the alcohol, 1-phenylethanol.

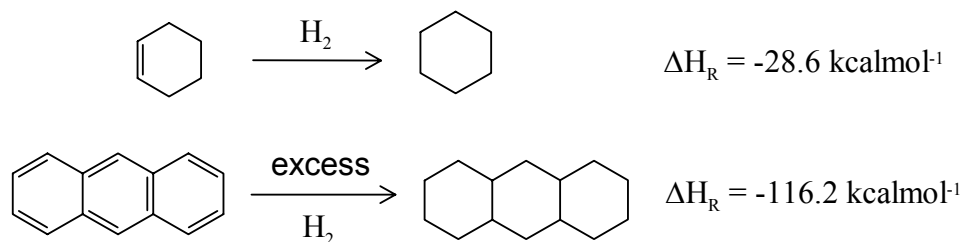
1. Protonation of the alkene in phenylethene (styrene) by sulphuric acid to give a stabilised carbocation.
2. Attack of water as a nucleophile on this carbocation to give an oxonium ion.
3. Abstraction of a proton from the oxonium by a base (eg H₂O) to produce 1-phenylethanol.

Draw a carbocation that is isomeric to the one produced in step (1) and that would result in the formation of 2-phenylethanol if steps (2) and (3) then occurred.

Explain using a short paragraph and / or diagrams why the carbocation that leads to 1-phenylethanol is preferred to the one that leads to 2-phenylethanol.

10 **PART 8: THERMODYNAMICS**

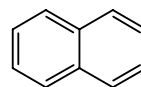
Write your answer in the booklet provided. Show your working as **PARTIAL** marks will be given.



Resonance Energies / kcalmol⁻¹

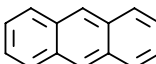


36

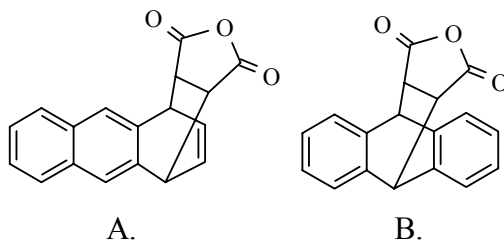


61

Using the data provided above, answer the following questions:

Calculate the resonance energy of anthracene, 

Anthracene is known to react with maleic anhydride in a Diels-Alder reaction to give only product B shown below, and not A. Using the **RESONANCE ENERGIES** explain using a short paragraph (1/2 page MAX) why this selectivity is observed.



****THE END****