

UNIVERSITY OF CALGARY
FACULTY OF CONTINUING EDUCATION
MIDTERM EXAMINATION
CHEMISTRY 351

JUNE 3rd, 1999.

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. 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 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**.

Value14 PART 1 RELATIVE PROPERTIES

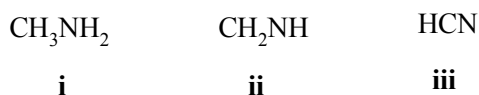
ANSWER ANY SEVEN (7) of Questions 1-8.

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 |

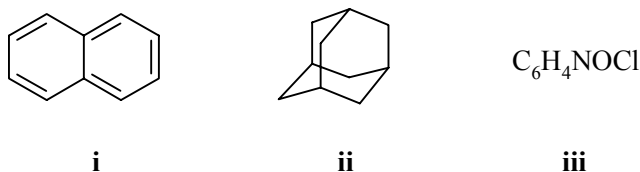
1. The H-C-N bond angles in each of the following:



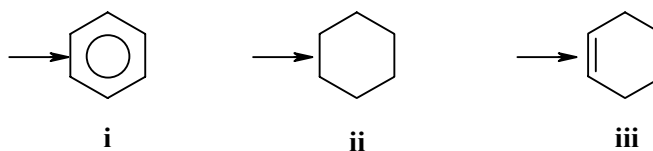
2. The heats of combustion, ΔH_c° of the following isomeric hydrocarbons (most endothermic to most exothermic):

- i** 2,2,3,3,4-pentamethylpentane
- ii** 3,4-diethylhexane
- iii** n-decane

3. The index of hydrogen deficiency (IHD) or $(\pi + r)$ of the following molecules:



4. The bond lengths of the indicated bonds in each of the following molecules:

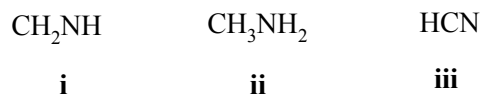


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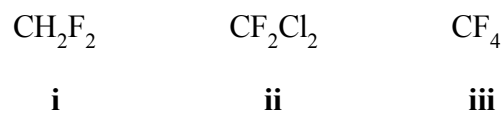
Use the following code to indicate your answers.

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

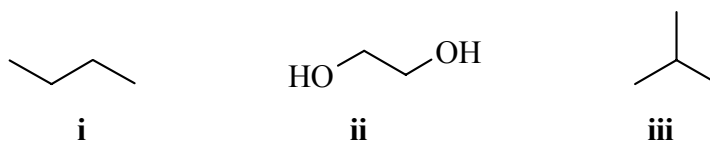
5. The % "s" character in the hybridised orbitals at the C atom in each of the following:



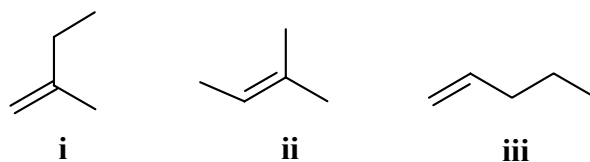
6. The molecular dipoles of each of the following:



7. The boiling points of the following:



8. The relative stability of the following isomeric alkenes:



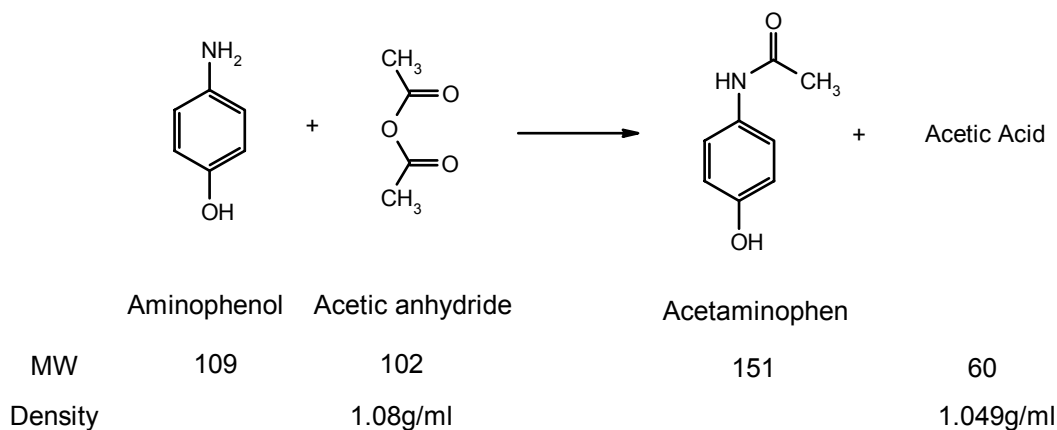
Value14 PART 2: LABORATORY**ANSWER ALL of the questions 9-18.**

For questions **9-14**, decide whether the whole statement is true or false. If it is **TRUE**, blacken A. If it is **FALSE**, then blacken B. (1 mark / question)

9. When recording the boiling point of a liquid it is important to correct to the sea level value for literature comparisons since boiling point increases with decreasing pressure.
10. When carrying out a distillation it is important to heat the distilling flask vigorously to ensure that the sample reaches equilibrium as rapidly as possible.
11. Traces of water in an organic solvent can be removed by adding a drying agent such as anhydrous magnesium sulphate.
12. When adding charcoal to removed coloured impurities, it should always be added to a near boiling solution for maximum efficiency.
13. During a fractional distillation, the condenser should be cooled by a gentle flow of water.
14. A saturated solution means that it cannot dissolve any more of the solute.

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Questions **15-18** (2 marks / question) refer to the following reaction scheme:



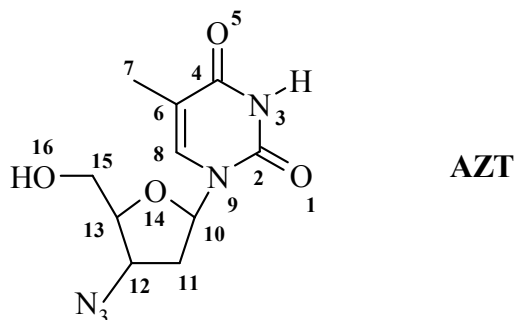
In the preparation of acetaminophen experiment, Sue Dent used 0.545g of aminophenol and 0.46ml of acetic anhydride, and obtained 0.73g of crude acetaminophen as large, off white lumps. After recrystallisation, Sue reported a 95% yield of crystalline, pure white acetaminophen.

Note 1 mmol = 0.001 mol

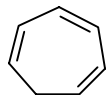
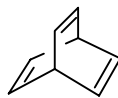
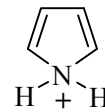
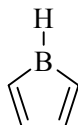
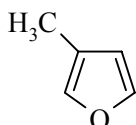
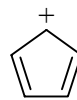
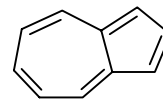
15. How many moles of the limiting reagent were used ?
- A. 4.2 mmol B. 4.6 mmol C. 5.0 mmol D. 43.4 mmol E. 45 mmol
16. What was the % yield of crude acetaminophen ?
- A. < 65% B. 65-75% C. 75-85% D. 85-95% E. >95%
17. Which of the following could explain the crude yield ? (more than one answer maybe correct, select all that are correct)
- A. The crude product contained some coloured impurities
 B. The crude product still contained acetic anhydride
 C. The crude product was still wet
 D. Sue had added too much aminophenol
18. How much pure acetaminophen did Sue obtain ?
- A. 0.55g B. 0.6g C. 0.66g D. 0.71g E. 0.73g

Value14 PART 3: MOLECULAR PROPERTIES**ANSWER ALL of the questions 19 - 25.**

For each of the questions **19 - 25** about the anti-AIDS drug AZT (see below), select the answer from those provided:



19. What is the oxidation state of **C4**?
- A. +3 B. +2 C. 0 D. -2 E. -3
20. Which of the following bond would be the shortest ?
- A. C4-C6 B. C6-C7 C. C6-C8 D. C10-C11 E. C13-C15
21. Which carbon is sp^3 hybridised ?:
- A. C2 B. C4 C. C6 D. C8 E. C11
22. What is the hybridisation of **N3** ?
- A. sp^4 B. sp^3 C. sp^2 D. sp E. sp^3d
23. The azide group (N_3) attached to **C12** is best represented as which of the following ?
- $\overset{+}{-}N-\overset{-}{N}\equiv N$
 $\overset{-}{N}=\overset{+}{N}=\overset{-}{N}$
 $\overset{-}{N}-\overset{+}{N}=\overset{-}{N}$
 $\overset{-}{N}=\overset{-}{N}=\overset{+}{N}$
 $\overset{+}{-}N\equiv N=\overset{-}{N}$
- A** **B** **C** **D** **E**
24. Which hydrogen is most acidic ? Designate this by selecting the atom to which the H is bonded.
- A. 3 B. 7 C. 8 D. 9 E. 16
25. What is the index of hydrogen deficiency (IHD) or $(\pi+r)$ of **AZT** ?
- A. 3 B. 4 C. 5 D. 6 E. 7

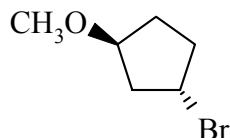
Value14 PART 4: AROMATICITY AND RESONANCE**ANSWER ANY SEVEN (7) of the questions 26-33.****A****B****C****D****E****AB****AC****AD****AE****BC**

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

26. A neutral, 4π -electron, anti-aromatic system.
27. A 6π -electron, aromatic system.
28. An aromatic system because $n=2$ in the Huckel $4n+2$ rule.
29. A non-aromatic, conjugated 6π -electron system
30. A non conjugated hydrocarbon.
31. Non-aromatic as drawn but on loss of a hydride ion gives an aromatic cation.
32. Non-aromatic as drawn, but has an important resonance structure that is aromatic.
33. Non-aromatic as drawn but has an aromatic conjugate base.

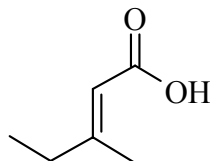
Value14 PART 5: NOMENCLATURE**ANSWER ANY SEVEN (7) of the questions 34-41.****For each of questions 34 to 41, select the correct name for the compound shown:**

34.



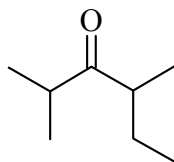
- A. *trans*-1-bromo-4-methylpentane
- B. *trans*-1-bromo-4-methoxycyclopentene
- C. *trans*-3-bromo-1-methoxycyclopentane
- D. *cis*-1-bromo-3-methoxycyclopentane
- E. 1-bromo-3-methoxycyclohexane

35.



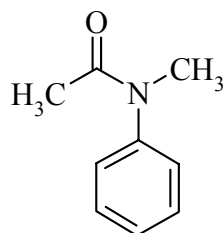
- A. (Z)-3-methyl-2-pentenoic acid
- B. (Z)-3-ethyl-2-butenic acid
- C. (E)-3-methyl-2-pentenoic acid
- D. (E)-3-ethyl-2-butenate
- E. (E)-3-ethyl-2-heptenoic acid

36.



- A. 2-ethyl-4-methyl-3-pentanone
- B. 4-ethyl-2-methyl-3-pentanone
- C. 3,5-dimethyl-4-hexanone
- D. 2,4-dimethyl-3-hexanone
- E. 2,4-dimethyl-4-hexanal

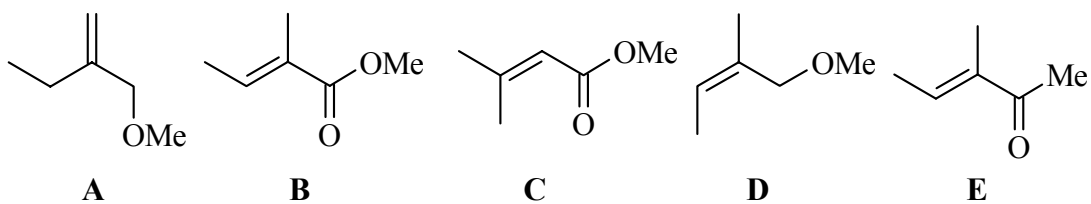
37.



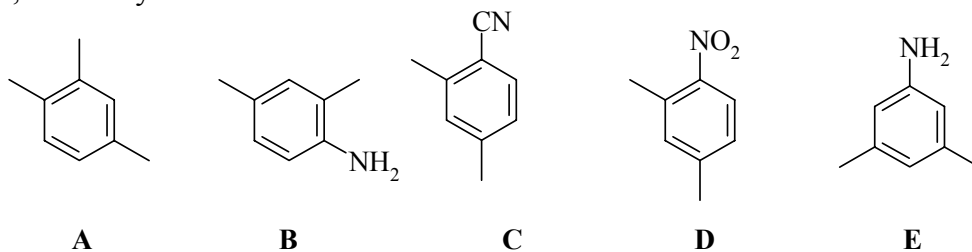
- A. N-methyl-N-phenylethanamine
- B. N,N-dimethylbenzylamine
- C. dimethylbenzamide
- D. N-methyl-N-phenylethanamide
- E. dimethylbenzamine

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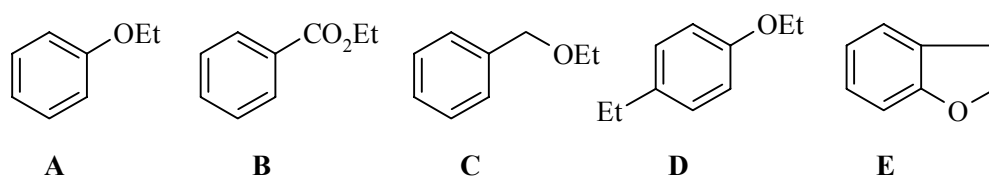
38. Methyl (E)-2-methyl-2-butenolate



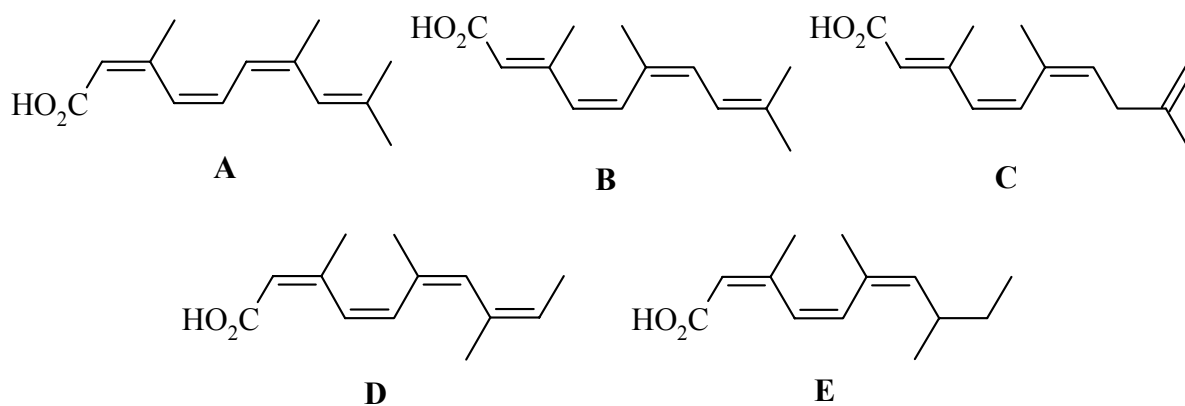
39. 2,4-dimethylnitrobenzene:



40. Ethyl benzoate:



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



Value9 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:

A combustion analysis was performed on a hydrocarbon sample from a railcar tanker spill. The result indicated that the sample contained 62.0% C and 10.4% H. The sample was further analysed and found to be a mixture of isomers and the empirical formula was the same as the molecular formula.

Use the combustion analysis data to determine the empirical formula.

What is the index of hydrogen deficiency (IHD) of the isomers ?

Draw the isomers (DO NOT INCLUDE CONFORMATIONAL ISOMERS)

Identify a pair of constitutional isomers, and name them.

Identify a pair of configurational isomers, and say which is E and which is Z.

List all the different functional groups that are present.

Value11 PART 7: MECHANISM and RESONANCE

Write your answer in the booklet provided.

Draw a sequence, using double headed (ie electron pair) curly arrows, that represents the events in the dehydration reaction of 1,2-dimethylcyclohexanol.

The processes involved are described by the following step-by-step points:

- Step 1:* Protonation of 1,2-dimethylcyclohexanol by sulphuric acid to give an oxonium ion.
Step 2: Loss of water from this species to form a stable carbocation.
Step 3: Show a generic base, B:, removing a proton from an sp^3 carbon atom in the carbocation to give 1,2-dimethylcyclohexene

Suggest two other alkenes that may have formed via loss of different protons.

Suggest why 1,2-dimethylcyclohexene is the major product.

Value10 PART 8: THERMODYNAMICS

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

Some thermodynamic data about cubane (see below) and phenylethene (styrene) is provided.

Cubane has a heat of combustion, $\Delta H_c = -1363.5$ kcal/mol. Phenylethene has a heat of formation, $\Delta H_f = 35.11$ kcal/mol. Knowing that the heats of combustion, ΔH_c , of carbon (graphite) = -94.05 kcal/mol and of hydrogen (gas) = -57.8 kcal/mol, calculate the heat of formation, ΔH_f , of cubane and the heat of combustion, ΔH_c , of phenylethene.

Draw an energy diagram that shows the relative stabilities of these two hydrocarbons.

Is it reasonable to compare the relative stabilities ?

Suggest a reason for the relative stability order.



Cubane

****THE END****