

THE UNIVERSITY OF CALGARY
FACULTY OF SCIENCE
MIDTERM EXAMINATION
CHEMISTRY 351

November 5th, 2008

Time: 2 Hours

READ THE INSTRUCTIONS CAREFULLY

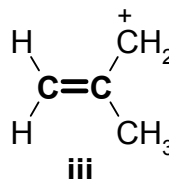
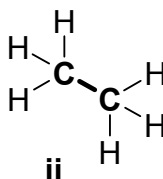
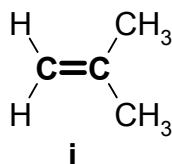
PLEASE WRITE YOUR **NAME, STUDENT I.D. NUMBER** ON **BOTH YOUR ANSWER BOOKLET AND COMPUTER ANSWER SHEET.**

The examination consists of Parts 1 - 7, each of which should be attempted. Note that some parts provide you with a choice of questions, e.g. 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 - 4 will be computer graded, and only Parts 5, 6, and 7 are to be answered in the booklet provided. A periodic table with atomic numbers and atomic weights is located inside the back cover.

Parts 1 - 4 consist of a series of multiple choice questions numbered 1 - 47 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**.

Absolutely no other electronic devices are allowed.

22% **PART 1: RELATIVE PROPERTIES****ANSWER ANY ELEVEN (11) of questions 1-15 (2 marks per question)**Arrange the items in **questions 1-15** 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 > i1. The relative lengths of the **BOLD** bonds in each of the following molecules:

2. The relative energies of the following orbitals of carbon:

p

isp³**ii**

sp

iii

3. The relative energies of the following molecular orbitals in ethene:

C C σ*

i

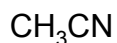
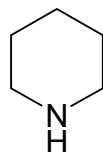
C C π*

ii

C C π

iii

4. The C-C-N bond angle in the following molecules:

**i****ii****iii**

Use the following code to indicate your answers.

A. i > ii > iii

B. i > iii > ii

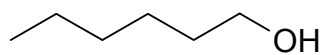
C. ii > i > iii

D. ii > iii > i

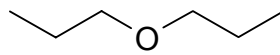
E. iii > i > ii

AB. iii > ii > i

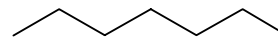
5. The boiling points of the following molecules:



i

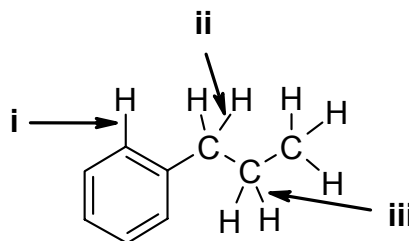


ii

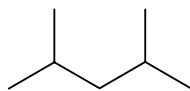


iii

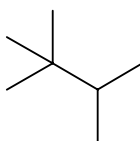
6. The relative strength of the CH bonds indicated in each of the following:



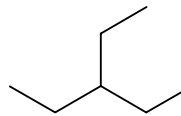
7. The relative stability of the following molecules:



i



ii



iii

8. The relative energies of the most stable conformations of the following cyclohexanes:

i cis-1,2-dimethylcyclohexane

ii cis-1,3-dimethylcyclohexane

iii trans-1,2-dimethylcyclohexane

9. The relative energy of the following conformations of cyclohexane:

Boat

i

Chair

ii

Twist-boat

iii

Use the following code to indicate your answers.

A. i > ii > iii

B. i > iii > ii

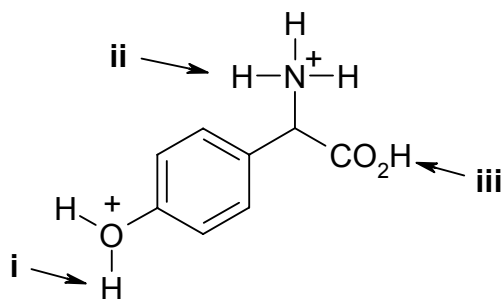
C. ii > i > iii

D. ii > iii > i

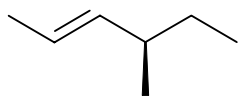
E. iii > i > ii

AB. iii > ii > i

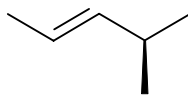
10. For the amino acid tyrosine, the relative pKa of the indicated proton:



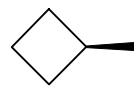
11. The number of possible stereoisomers of the following:



i

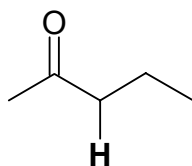


ii

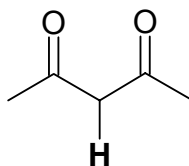


iii

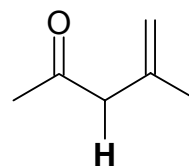
12. The relative acidity of the protons in **bold**:



i

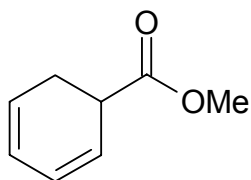


ii

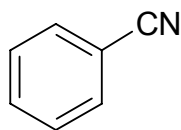


iii

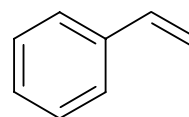
13. The relative IHD of the following molecules:



i



ii



iii

Use the following code to indicate your answers.

A. i > ii > iii

B. i > iii > ii

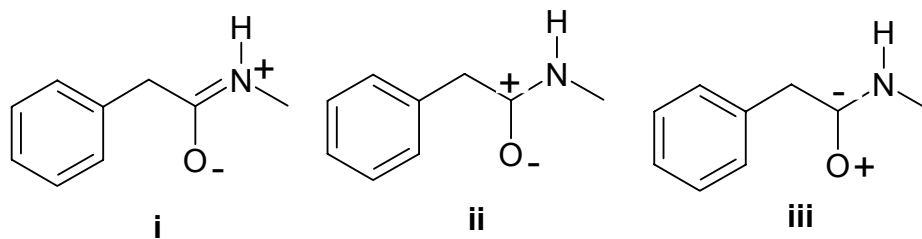
C. ii > i > iii

D. ii > iii > i

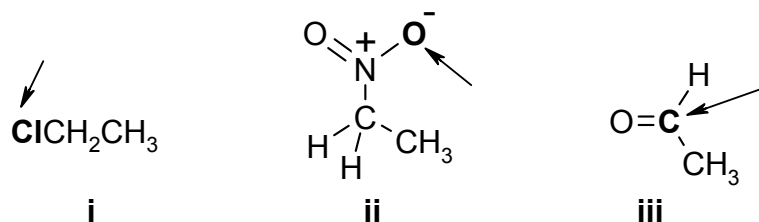
E. iii > i > ii

AB. iii > ii > i

14. The relative importance of the following resonance structures of an amide:



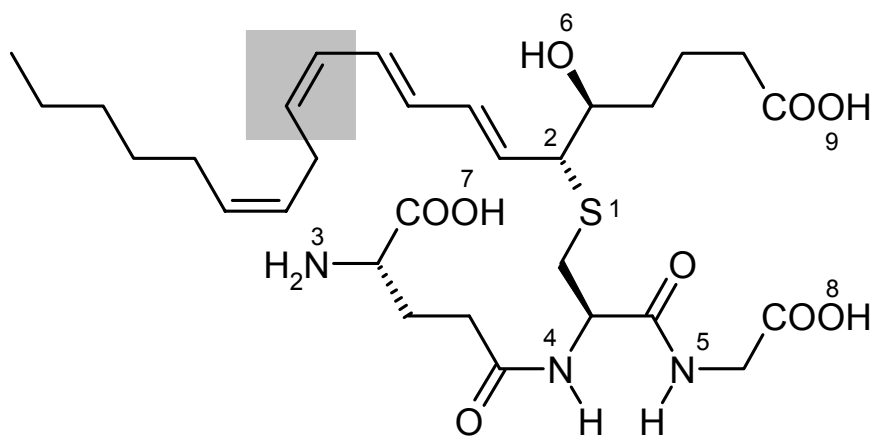
15. Oxidation state of the indicated **BOLD** atoms in each of the following molecules:



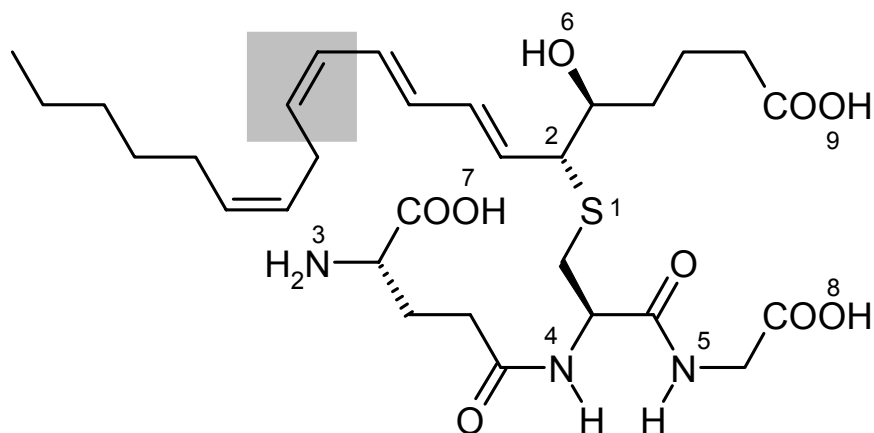
18% **PART 2: MOLECULAR PROPERTIES**

ANSWER ALL of the questions 16-27 (1.5 marks per question)

The questions 16- 27 are about Leukotriene C₄ (shown below), a molecule which acts as a smooth muscle constrictor.



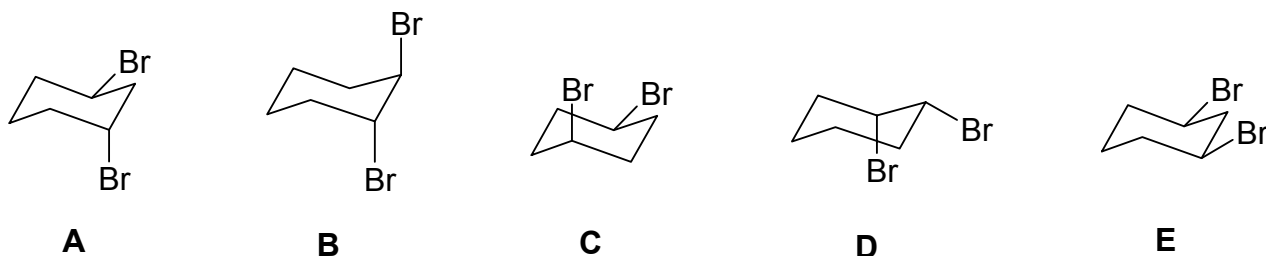
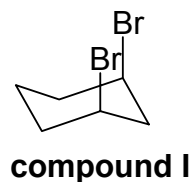
16. What is the C-S-C bond angle for **S1** ?
 A. 90° B. 180° C. 109.5° D. 120° E. 112°
17. What is the configuration at **C2** ?
 A. E B. 3 C. R D. S E. Z
18. Which of the following is/are an amine ?
 A. N3 B. N4 C. N5 D. S1 E. None
19. Which atom is the most basic ?
 A. N3 B. N4 C. N5 D. O6 E. S1
20. The proton attached to which of the following atom has the **highest** pKa value ?
 A. C2 B. O6 C. O7 D. O8 E. O9
21. For **N3**, what is the **H-N-H** bond angle ?
 A. 90° B. 180° C. 109.5° D. 120° E. 112°
22. What are the hybridizations of **S1 / O6** ?
 A. sp³ / sp³ B. sp³ / sp² C. sp² / sp² D. sp / sp E. sp / sp³



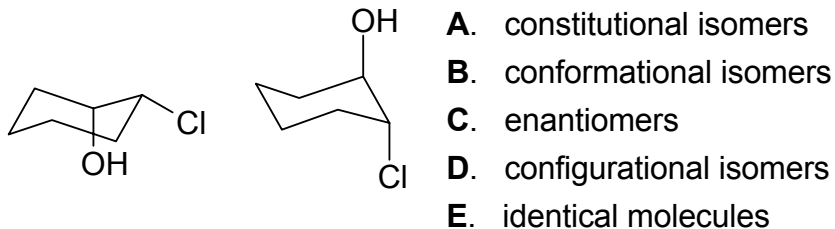
23. What is the IHD of Leukotriene C₄ ?
 A. 4 B. 6 C. 8 D. 9 E. 12
24. How many sp² hybridized carbon atoms are there in Leukotriene C₄ ?
 A. 8 B. 10 C. 13 D. 16 E. 17
25. What word(s) can be used to describe the functional group in the shaded square ?
 A. Alkene B. Alkyne C. Conjugated D. Cumulated E. Isolated
26. In what type of functional group is **N4** involved ?
 A. Amide B. Amile C. Amine D. Imine E. Nitrile
27. What is the oxidation state of **N4** ?
 A. +3 B. +1 C. 0 D. -1 E. -3

12% **PART 3: CONFORMATIONAL ANALYSIS****ANSWER EIGHT of the questions 28-36 (1.5 marks per question).**28. How many equatorial hydrogens are there in the most stable conformation of *cis*-1,3-dimethylcyclohexane?

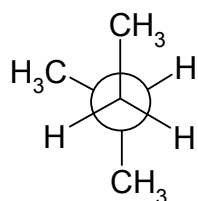
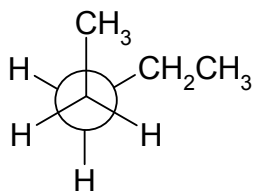
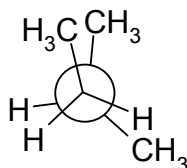
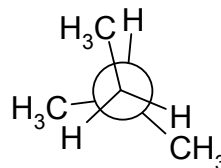
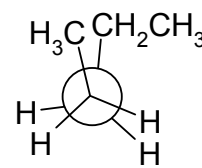
- A. 10
 B. 6
 C. 5
 D. 4
 E. 3

29. Which of the following is a conformational isomer of **compound I** ?

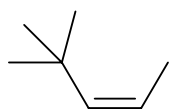
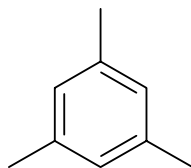
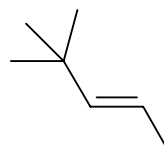
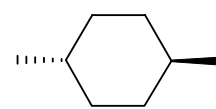
30. What best describes the relationship between the two compounds shown below ?



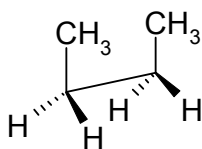
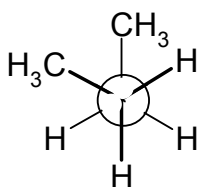
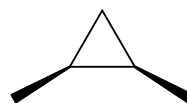
31. On an energy diagram showing the conformations of *n*-pentane, which of the following would be an energy maximum ?

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

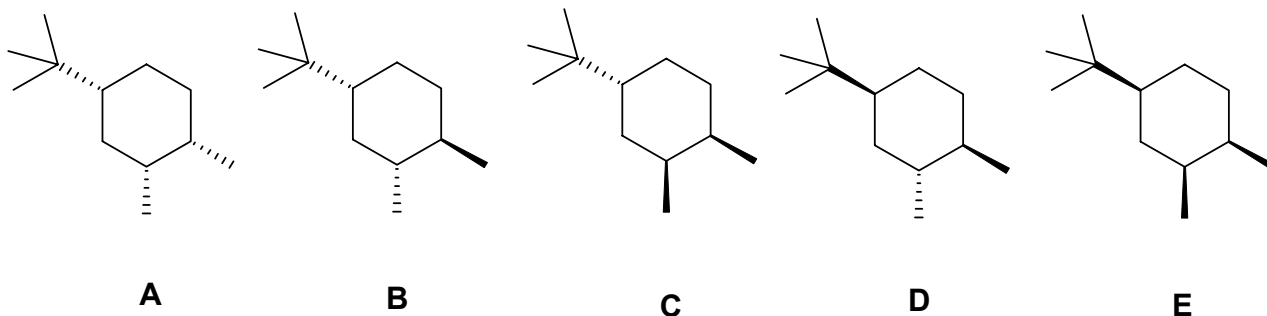
32. Which of the following has the most van der Waals strain ?

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

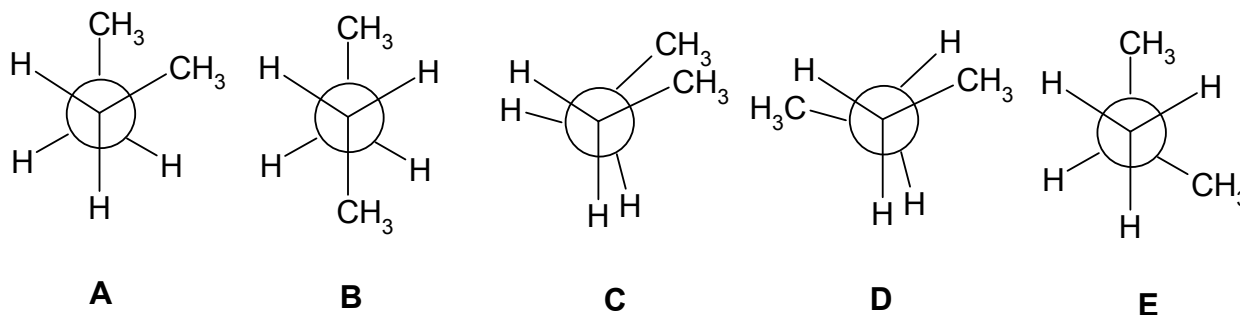
33. Which of the following has the least torsional strain ?

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

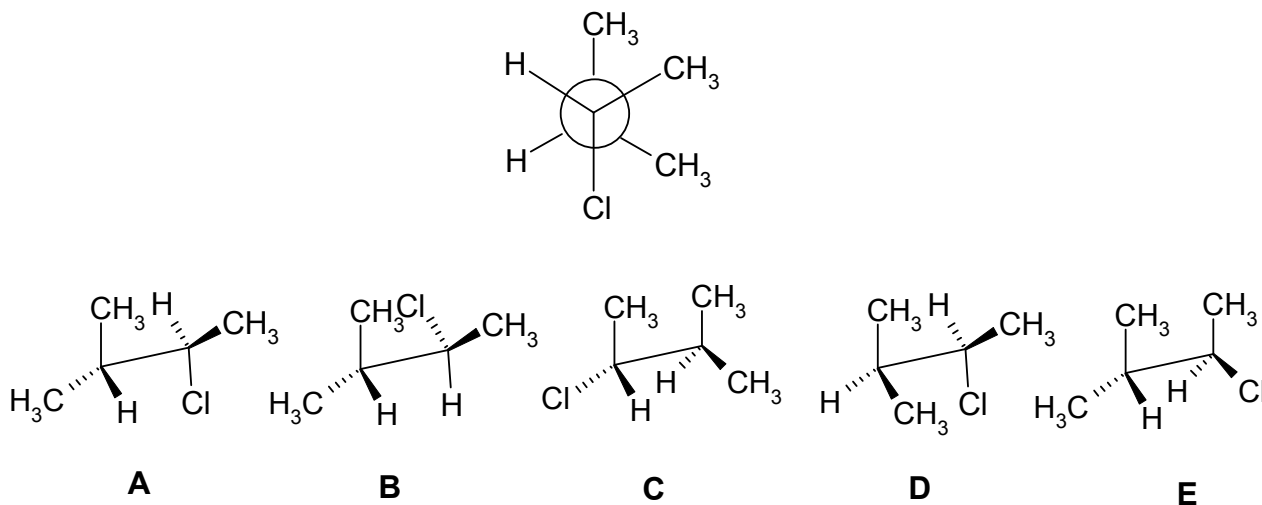
34. Which of the following cyclohexane molecules has the largest torsional angle between its two methyl groups ?



35. Which of the following conformations of butane will be the most populated at any given time ?

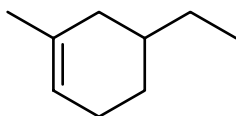


36. Which of the following molecules has the same conformation as the 2-chloro-3-methylbutane isomer shown as a Newman projection:



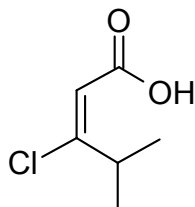
15% **PART 4: NOMENCLATURE****ANSWER ANY TEN (10) of the questions 37-48 (1.5 marks per question).****For each of questions 37 to 41, select the correct name for the compound shown:**

37.



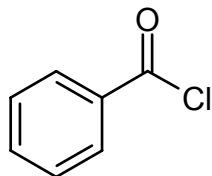
- A. 1-Methyl-3-ethylcyclohexene
- B. 1-Methyl-5-ethylcyclohexene
- C. 2-Methyl-4-ethylcyclohexene
- D. 3-Ethyl-1-methylcyclohexene
- E. 4-Ethyl-2-methylcyclohexene

38.



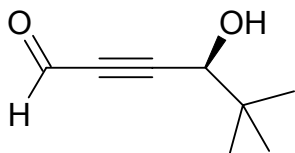
- A. (Z)-3-Chloro-4-methyl-2-pentenoic acid
- B. (E)-3-Chloro-4-methyl-2-pentenoic acid
- C. (Z)-3-Chloro-3-isopropyl-2-propenoic acid
- D. (E)-3-Chloro-3-isopropyl-2-propenoic acid
- E. (Z)-4-Methyl-3-chloro-2-pentenoic acid

39.



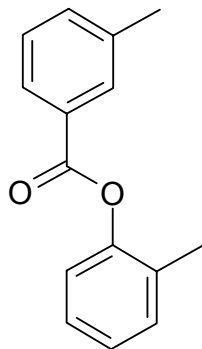
- A. Benzoyl chloride
- B. Benzyl chloro ketone
- C. Chlorobenzaldehyde
- D. Chloro benzyl ketone
- E. Chloro phenyl ketone

40.



- A. (R)-4-Hydroxy-5,5-dimethylhexanal
- B. (S)-2,2-Dimethyl-6-oxohex-4-yn-3-ol
- C. (R)-2,2-Dimethyl-6-oxohex-4-yn-3-ol
- D. (S)-4-Hydroxy-5,5-dimethylhex-2-ynal
- E. (R)-4-Hydroxy-5,5-dimethylhex-2-ynal

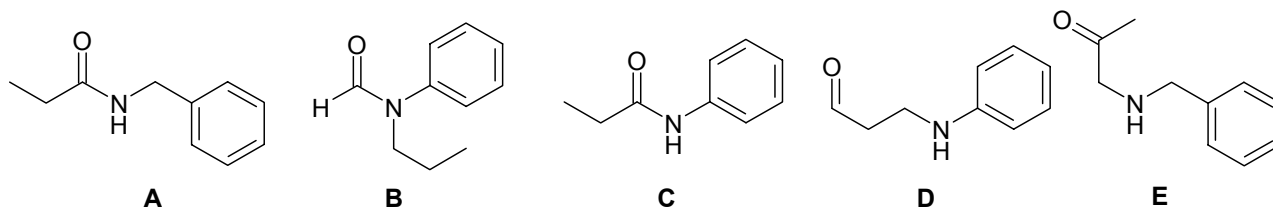
41.



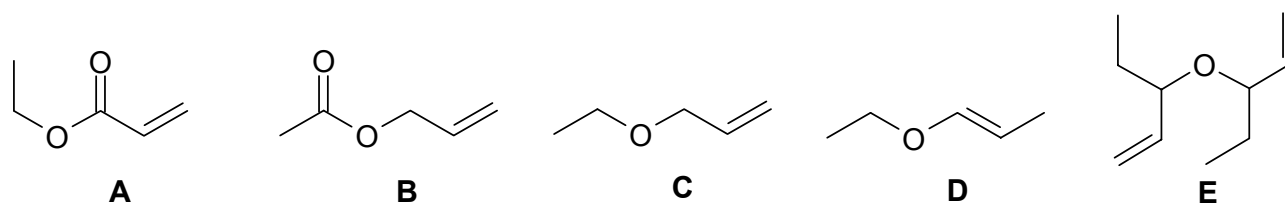
- A. 2,3-dimethylphenyl benzoate
- B. 2,3-dimethylphenoxybenzaldehyde
- C. 2-methylphenoxy-3-methylphenylketone
- D. 2-methylphenyl 3-methylbenzoate
- E. ortho,meta-dimethylphenyl benzoate

For each of questions 42 to 47, select the correct structure for the name provided:

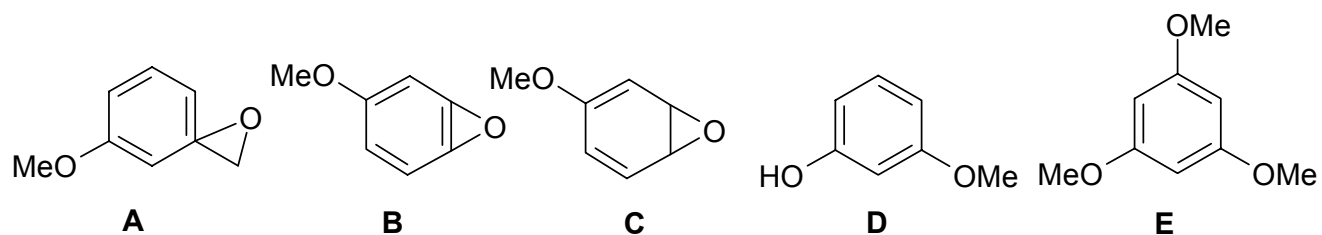
42. *N*-benzylpropanamide

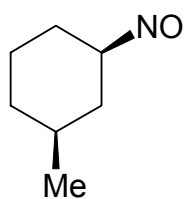
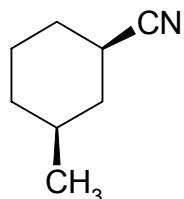
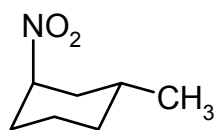
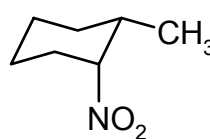
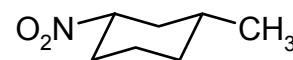
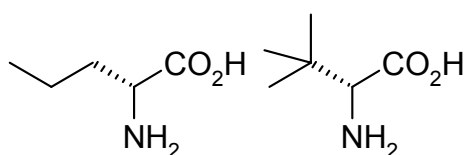
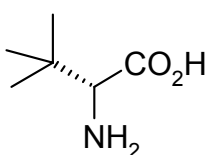
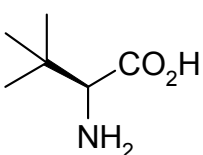
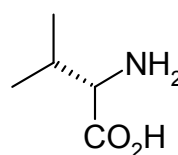
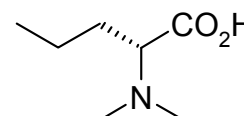
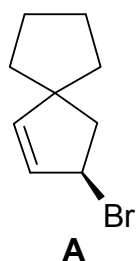
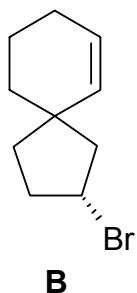
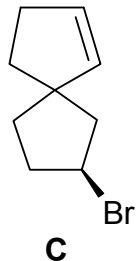
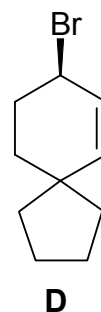
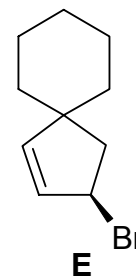


43. Ethyl 2-propenyl ether



44. 3-Methoxyphenol



45. *cis*-3-methyl-1-nitrocyclohexane**A****B****C****D****E**46. (*S*)-2-amino-3,3-dimethylbutanoic acid**A.****B.****C.****D.****E.**47. (*R*)-3-bromospiro[4.5]dec-1-ene**A****B****C****D****E**

10% PART 5: 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 sample of an unknown liquid was analyzed by GC-MS to show a single peak and have a molecular weight of 79. The molecule was found to be basic, the pKa of its conjugate acid was found to be about 5. The sample was further analyzed by elemental analysis to reveal that it contains 75.95% C, 6.33% H and 17.72% N.

- (a). Determine the molecular formula.
- (b). What is the IHD of the molecule ?
- (c). Propose a valid structure that match the chemical properties.
- (d). How many "types" of carbon are in the molecule proposed in part (c) ?
- (e). Draw a molecule that fits the molecular formula that contains a chiral center, and thus would have an enantiomer.
- (f). Draw one more molecule that fits the molecular formula and is a constitutional (structural) isomer of the molecules proposed in parts (c) and (e).

12% **PART6: MECHANISM**

Write your answer in the booklet provided. For FULL marks you MUST show your working. PARTIAL marks will be awarded.

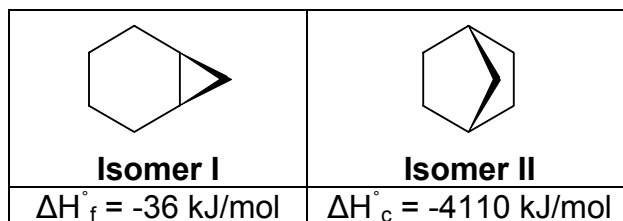
Draw a mechanism sequence using double headed (i.e. electron pair) curly arrows that represents the single reaction sequence described verbally by the following points in which 1,3-butadiene is treated with hydrobromic acid (HBr) to give two products: 3-bromo-1-butene and 1-bromo-2-butene.

- (a) Attack of one of the double bonds of 1,3-butadiene on hydrobromic acid generates a resonance stabilized carbocation and a bromide ion.
- (b) Draw a resonance (hybrid) structure of the intermediate carbocation to show the two possible electrophilic centres (*i.e.* two possible carbocations).
- (c) Attack of the bromide anion on the electrophilic centre of one of the resonance structures produces the 3-bromo-1-butene, and attack of the bromide anion on the electrophilic center of a different resonance structure produces the 1-bromo-2-butene.
- (d) The product that was formed from the most stable carbocation was produced in a 70% yield, and the other product in 30% yield. Assign the percentage yield to each product and explain your reasoning in detail.
- (e) Draw the stereoisomers of both products and give complete IUPAC name for each of them.
- (f) What is the relationship between the 1-bromo-2-butene isomers ? What is the relationship between the 3-bromo-1-butene isomers ? What is the relationship between 1-bromo-2-butene and 3-bromo-1-butene ?
- (g) Based on the above mechanism, if you react 1,3-butadiene with hydrobromic acid in the presence of Sodium Chloride, what other products could form? Draw the structures of the products (you don't need to show the mechanism for the formation of these products).

11% **PART 7: THERMODYNAMICS**

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

Refer to the following two structures to answer the questions below.



- i. What type of isomers are **I** and **II** ?
- ii. Are either of these molecules chiral ?
- iii. Given the heats of combustion for graphite, $\Delta H_c^\circ, C_{(\text{graphite})} = -393.5 \text{ kJ/mol}$, and for hydrogen, $\Delta H_c^\circ, H_{2(g)} = -241.8 \text{ kJ/mol}$, calculate ΔH_c° for **Isomer I** and ΔH_f° for **Isomer II**.
- iv. Which isomer is more stable? (Use an energy diagram to illustrate)
- v. Justify your choice in **part iv** by highlighting the types of strain that may be present in both molecules.
- vi. Draw any other isomer of the molecules **I** and **II**.

**** THE END ****

PERIODIC TABLE

1																18				
1A																8A				
1 H 1.008	2										13	14	15	16	17	2				
	2A										3A	4A	5A	6A	7A	He 4.003				
3 Li 6.941	4 Be 9.012											5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18			
11 Na 22.99	12 Mg 24.31	3	4	5	6	7	8	9	10	11	12	13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.07	17 Cl 35.45	18 Ar 39.95			
19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.88	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.69	29 Cu 63.55	30 Zn 65.38	31 Ga 69.72	32 Ge 72.59	33 As 74.92	34 Se 78.96	35 Br 79.90	36 Kr 83.80			
37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.94	43 Tc (98)	44 Ru 101.1	45 Rh 102.9	46 Pd 106.4	47 Ag 107.9	48 Cd 112.4	49 In 114.8	50 Sn 118.7	51 Sb 121.8	52 Te 127.6	53 I 126.9	54 Xe 131.3			
55 Cs 132.9	56 Ba 137.3	57* La 138.9	72 Hf 178.5	73 Ta 180.9	74 W 183.9	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.1	79 Au 197.0	80 Hg 200.6	81 Tl 204.4	82 Pb 207.2	83 Bi 209.0	84 Po (209)	85 At (210)	86 Rn (222)			
87 Fr (223)	88 Ra 226.0	89** Ac (227)	104 Rf (261)	105 Ha (262)	106 Sg (263)	107 Ns (262)	108 Hs (265)	109 Mt (266)	110 Uun (269)	111 Uuu (272)										

Lanthanides *

58 Ce 140.1	59 Pr 140.9	60 Nd 144.2	61 Pm (145)	62 Sm 150.4	63 Eu 152.0	64 Gd 157.3	65 Tb 158.9	66 Dy 162.5	67 Ho 164.9	68 Er 167.3	69 Tm 168.9	70 Yb 173.0	71 Lu 175.0
90 Th 232.0	91 Pa 231.0	92 U 238.0	93 Np 237.0	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (252)	100 Fm (257)	101 Md (258)	102 No (259)	103 Lr (260)

Actinides **