THE UNIVERSITY OF CALGARY

FACULTY OF SCIENCE

FINAL EXAMINATION

CHEMISTRY 351

DECEMBER 17th 2001 Time: 3 Hours

READ ALL THE INSTRUCTIONS CAREFULLY

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

The examination consists of Parts 1 - 9, 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 completed, regardless of whether they are right or wrong. Parts 1 - 5 will be computer graded, and Parts 6 - 9 are to be answered in the answer booklet provided. A periodic table with atomic numbers and atomic weights, and spectroscopic tables are appended to this examination paper.

Parts 1 - 5 consist of a series of multiple choice questions numbered 1 - 43, 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***.

PART 1 RELATIVE PROPERTIES

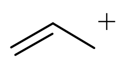
20% **ANSWER ANY TEN (10) OF QUESTIONS 1 TO 14.**

Arrange the items in questions 1-14 in DECREASING ORDER (i.e. greatest, most etc. first) with respect to the indicated property.

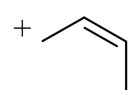
Use the following code to indicate your answers.

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 stability of the following carbocations:



i



ii

$\overset{+}{C}H_3$

iii

2. The relative nucleophilicity of the following in a polar, protic solvent:

$CH_3CH_2O^-$	H_2O	NH_3
i	**ii**	**iii**

3. The relative acidity of the most acidic hydrogen in each of the following:

CH_3CH_2OH	CF_3CH_2OH	$CH_3CH_2NH_2$
i	**ii**	**iii**

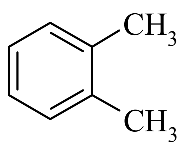
4. The relative energies of the following molecular orbitals in the bonding of ethene:

σ CH	π CC	π^* CC
i	**ii**	**iii**

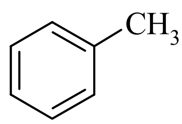
Use the following code to indicate your answers.

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

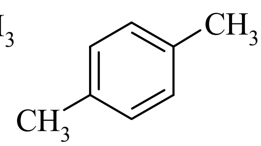
5. The number of peaks seen in the normal broadband proton decoupled 13C nmr spectrum for each of the following:



i



ii

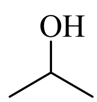


iii

6. The relative rate of reaction of each of the following with NaI in acetone:

$(CH_3)_2CHCl$

i



ii

CH_3CH_2Br

iii

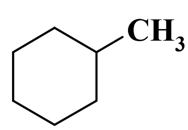
7. The number of peaks seen in the H nmr spectra coupling pattern corresponding to the group in **bold** in each of the following:

$CH_3CH_2\mathbf{CH_2}CH_2CH_3$

i

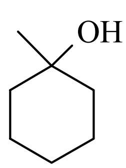
$CH_3\mathbf{CH_2}CH_2CH_3$

ii

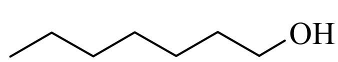


iii

8. The relative rates of reaction of each of the following with conc. H_2SO_4 :



i



ii

3-pentanol

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**

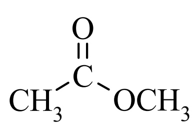
9. The relative strengths of the H-X bonds in each of the following :

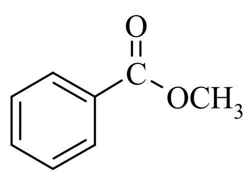
H−I	H−F	H−O−H
i	**ii**	**iii**

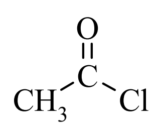
10. The relative importance of the following resonance contributors to CH_3CNO :

$CH_3{-}C{\equiv}\overset{+}{N}{-}\overset{-}{O}$	$CH_3{-}\overset{-}{C}{=}\overset{+}{N}{=}O$	$CH_3{-}C{\equiv}N{=}O$
i	**ii**	**iii**

11. The bond stretching frequencies / cm^{-1} in the infra-red spectrum for the carbonyl group in each of the following:


i


ii


iii

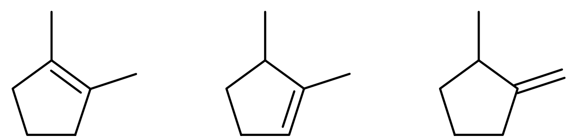
12. The relative rates of reaction of each of the following with HBr:

$CH_3(CH_2)_6OH$	$(CH_3CH_2)_3COH$	4-heptanol
i	**ii**	**iii**

Use the following code to indicate your answers.

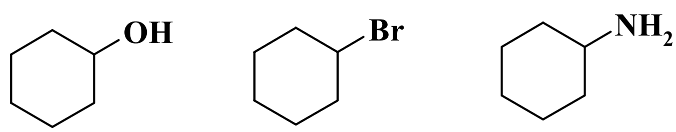
A.	**i > ii > iii**	**D.**	**ii > iii > i**
B.	**i > iii > ii**	**E.**	**iii > i > ii**
C.	**ii > i > iii**	**AB.**	**iii > ii > i**

13. The heats of hydrogenation of the following alkenes (most endothermic to most exothermic):



i **ii** **iii**

14. The ability of the group in **bold** to be substituted:



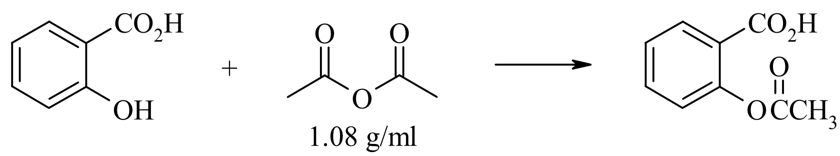
i **ii** **iii**

PART 2: LABORATORY

10% **ANSWER ALL FIVE (5) OF THE QUESTIONS 15-19.**

Questions 15-19 are based on the laboratory component of the course.
In each case select ALL of the statements that are true.
In SOME questions, MORE THAN ONE STATEMENT MAY BE CORRECT.

15. If 1.381g of salicylic acid was reacted with 1.5ml of acetic anhydride to give 1.621g crude aspirin, then what is the % yield of crude aspirin ?



A 57% **B** 61% **C** 85% **D** 90% **E** 95%

16. In the experiment about the reactivity of alcohols, which of the following statements are true ?

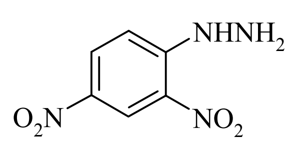
A the tertiary alcohols were oxidised to ketones.

B chromic acid H_2CrO_4 contains Cr VI.

C the relative reactivity towards substitution with $HCl/ZnCl_2$ was $1^o > 2^o > 3^o$.

D the layer that forms in the Lucas test is the alkyl chloride.

E 2,4-dinitrophenylhydrazine (or 2,4-DNP) has the following structure:



17. In the experiment about the reactivity of alcohols, which of the following statements about the reagent bromine in chloroform are true ?

A the reaction of the bromine is an example of an addition reaction

B the product of the reaction is a colourless 1,2-dibromide

C the bromine reacts with the alkene formed by dehydration of the alcohol

D chloroform has the molecular formula CH_2Cl_2.

E All molecules with the formula C_4H_8 would give a positive test

18. In the experiment about the reactivity of alkyl halides, which of the following statements about the reactions with NaI / acetone are true ?

A acetone is an example of a polar, protic solvent.

B t-butyl chloride is $(CH_3)_3CCl$.

C this is an example of SN1 reaction.

D the precipitate that forms is the alkyl iodide.

E bromine is a better leaving group than chorine.

19. In the experiment about the reactivity of alkyl halides, which of the following statements about the reactions with $AgNO_3$ / aq. ethanol are true ?

A bromides were more reactive than similar chlorides.

B if ethanol reacts as a nucleophile, the product is an ester.

C silver nitrate is used to enhance the nucleophilicity of the water.

D the primary chloride reacted rapidly under these conditions.

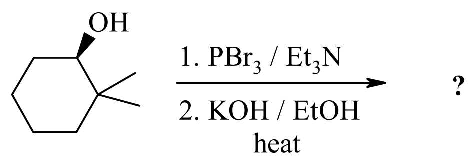
E the solvent is polar and so favours the carbanion intermediate.

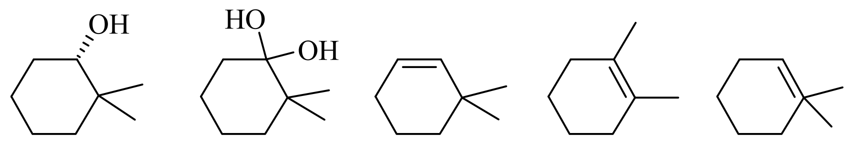
PART 3: REACTIONS

14% **ANSWER ANY SEVEN (7) OF QUESTIONS 20-27.**

For each of questions 20-27 select either the major product or the starting material required in order to complete each of the reaction schemes

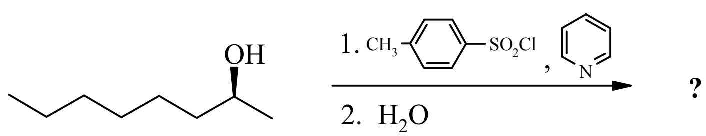
20.

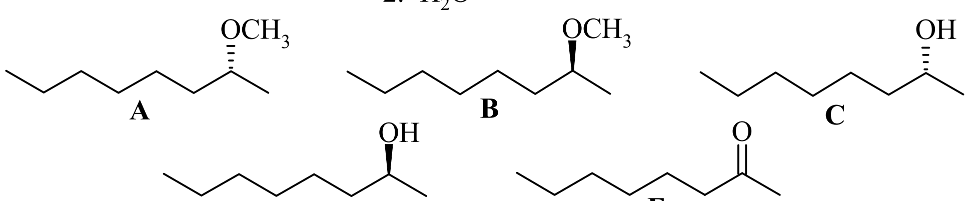




A **B** **C** **D** **E**

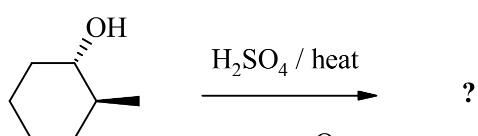
21.

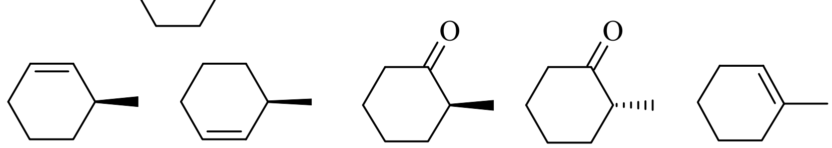




A **B** **C** **D** **E**

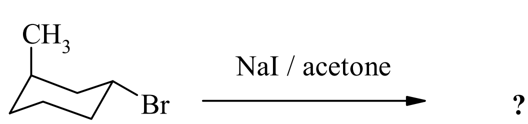
22.

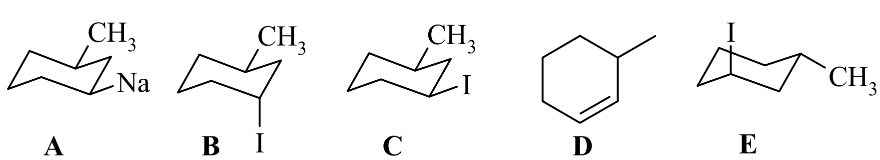




A **B** **C** **D** **E**

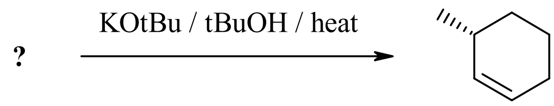
23.

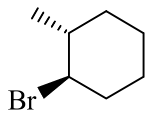


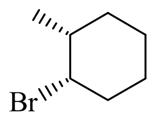


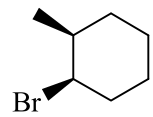
A **B** **C** **D** **E**

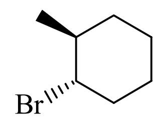
24.

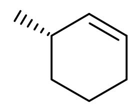



A

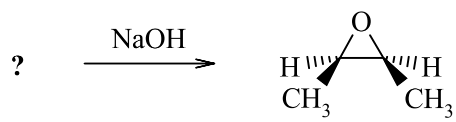

B

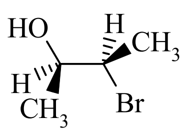

C

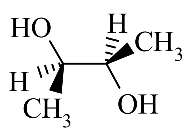

D


E

25.




A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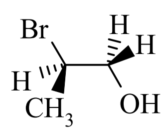
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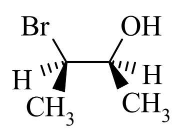
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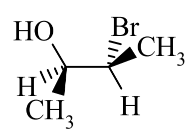
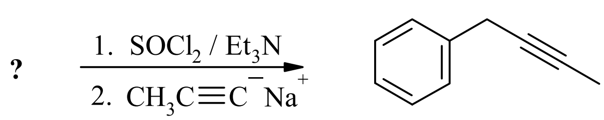
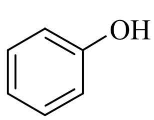
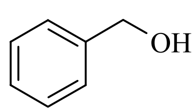

E

26.




A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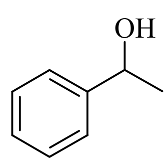
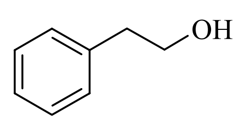
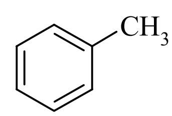
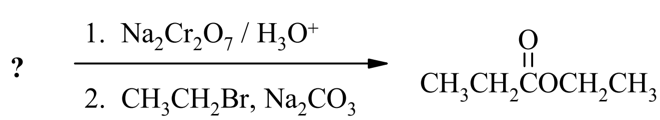
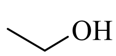

C

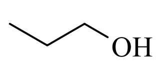

D

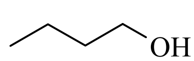

E

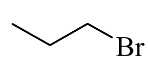
27.

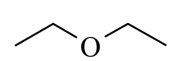



A


B


C


D

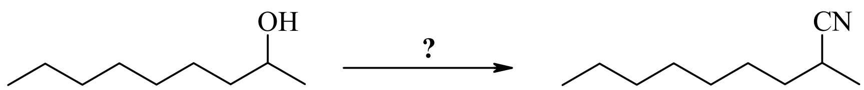

E

PART 4: REAGENTS FOR REACTIONS

10% **ANSWER ANY FIVE (5) OF QUESTIONS 28 -33.**

For each of questions 28-33 select the best reagent in order to complete each of the reaction schemes.

28.



A NaCN / DMSO

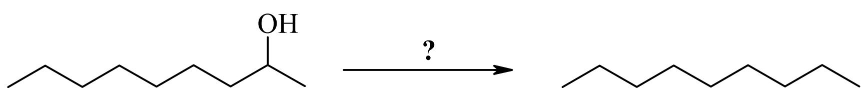
B NH_4Cl

C CH_3NH_2

D 1. TsCl / Et_3N
2. NaCN / DMSO

E 1. H_2SO_4 / heat
2. NaCN / DMSO

29.



A conc. H_2SO_4 / heat

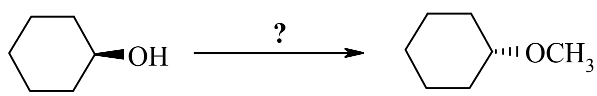
B KOH / EtOH / heat

C 1. H_2SO_4 / heat
2. H_2 / Pd

D 1. KOH / EtOH / heat
2. H_2 / Pd

E H_3O^+ / heat

30.



A CH_3OCH_3

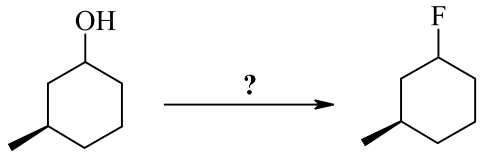
B CH_3OH / heat

C 1. Na 2. CH_3I

D 1. PBr_3 / Et_3N
2. $NaOCH_3$ / CH_3OH

E $NaOCH_3$ / CH_3OH

31.



A F_2

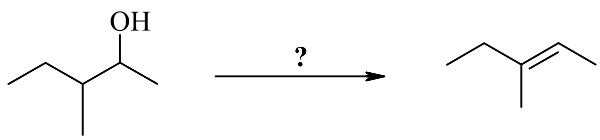
B aq. HF

C NaF / DMSO

D 1. TsCl / Et_3N
2. NaF / DMSO

E 1. TsCl / Et_3N
2. DMF

32.



A conc. H_2SO_4 / heat

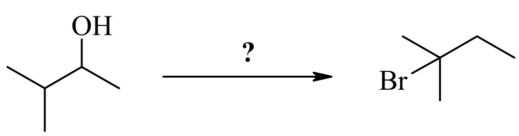
B KOH / EtOH / heat

C KOtBu / DMSO / heat

D 1. HBr
2. KOtBu / tBuOH / heat

E 1. TsCl / Et_3N
2. KOtBu / DMSO / heat

33.



A Br_2 / $CHCl_3$

B HBr

C PBr_3 / Et_3N

D NaBr / DMSO

E NaBr / KOH

PART 5: MECHANISMS

8% **ANSWER ANY EIGHT (8) OF QUESTIONS 34 -43.**

For each of questions 34-43 select the single term from the list provided below that corresponds BEST with each phrase.

A	electrophile	**AB**	concerted	**BD**	atomic polarisability
B	nucleophile	**AC**	stepwise	**BE**	Hoffmann
C	leaving group	**AD**	steric effect	**CD**	Walden
D	carbocation	**AE**	resonance	**CE**	Williamson
E	carbanion	**BC**	hyperconjugation	**DE**	Zaitsev

34. why *trans* acyclic alkenes are more stable than *cis*

35. the role of a halogen in an elimination reaction

36. a reaction pathway with several stages

37. the preferential formation of the more highly substituted alkene in an elimination

38. an intermediate in the E1 reaction of an alkyl halide

39. a factor contributing to the stability of $(CH_3)_3C^+$

40. reaction of an alcohol with sodium then an alkyl halide

41 a species prone to rearrangement

42. why t-butoxide is a poorer nucleophile than hydroxide

43. why thiols are more acidic than alcohols

PART 6: SYNTHESIS

9% **DESIGN EFFICIENT SYNTHESES OF ANY THREE (3) of the following target molecules using any of the starting materials shown below.**

WRITE YOUR ANSWERS IN THE BOOKLET PROVIDED.

DO NOT SHOW MECHANISMS.

TARGETS

2-butanol

trans-2-butene

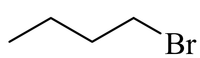
butane

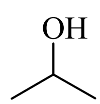
$(CH_3CH_2CH_2CH_2)_2O$

$(CH_3)_2CHCH_2CH_3$

$(CH_3)_2CHNH_2$

Allowed Starting Materials:





any compound with 2 or less C atoms

In addition you may use any solvents and /or inorganic reagents required.

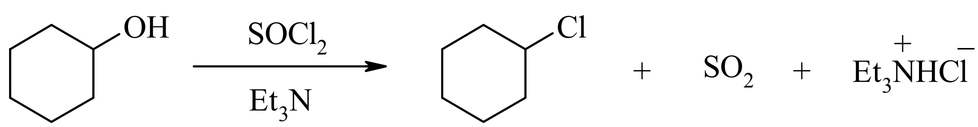
PART 7: MECHANISMS

9% **WRITE YOUR ANSWERS IN THE BOOKLET PROVIDED**

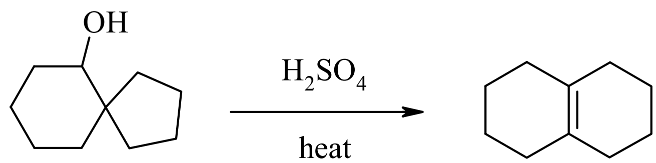
ANSWER ANY THREE (3) OF THE QUESTIONS I to IV.

Use curly arrow mechanisms to explain any three (3) of the following reactions / observations:

I.

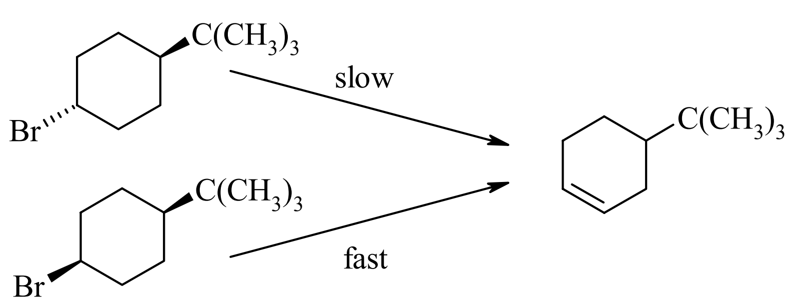


II.



III. Explain why 1-bromo-2-butene and (chloromethyl)benzene react rapidly via *both* SN1 and SN2 reaction pathways.

IV. Why do the following systems react with KOtBu at such different rates ?



PART 8: STRUCTURE DETERMINATION

10% **WRITE YOUR ANSWERS IN THE BOOKLET PROVIDED**

Compound **A**, $C_4H_{10}O$, (IR absorption : 3500 cm^{-1}, broad) reacted at a moderate rate with dry HCl give **B**, C_4H_9Cl. **A** when reacted with hot, conc. H_2SO_4 gave a hydrocarbon **C**, C_4H_8 (IR absorption : 1650 cm^{-1}) as the major product. When **A** was reacted with an acidic chromate solution, **D**, C_4H_8O (IR absorption : 1715 cm^{-1}) was obtained.

When **B** was heated with KOH / EtOH it also gave hydrocarbon **C**, but when **B** was heated with KOtBu / DMSO, the major product was **E**, a constitutional isomer of **C**. Reaction of **B** with H_2O / Na_2CO_3 gave **A**.

F, an isomer of **A**, was also reacted with hot concentrated H_2SO_4 giving a new hydrocarbon **G** that was a constitutional isomer of both **C** and **E**.

Catalytic hydrogenation of **C** and **E** gave the same alkane, but **G** gave an isomeric alkane.

In a ^{13}C nmr spectroscopic analysis of the compounds, **A**, **B**, **D** and **E** each had 4 peaks, **C** and **F** each had 2 peaks and **G** had 3 peaks.

- **Identify the compounds A-G.**

H nmr spectral data for **two** of the compounds **A-G** is listed below.

- **Match the spectral data to the appropriate compounds.**

I 2.4ppm, quartet, 2H; 2.1ppm, singlet, 3H; 1.0ppm, triplet, 3H

II 2.0ppm, broad singlet, 1H (exchanges with D_2O); 1.3ppm, singlet, 9H

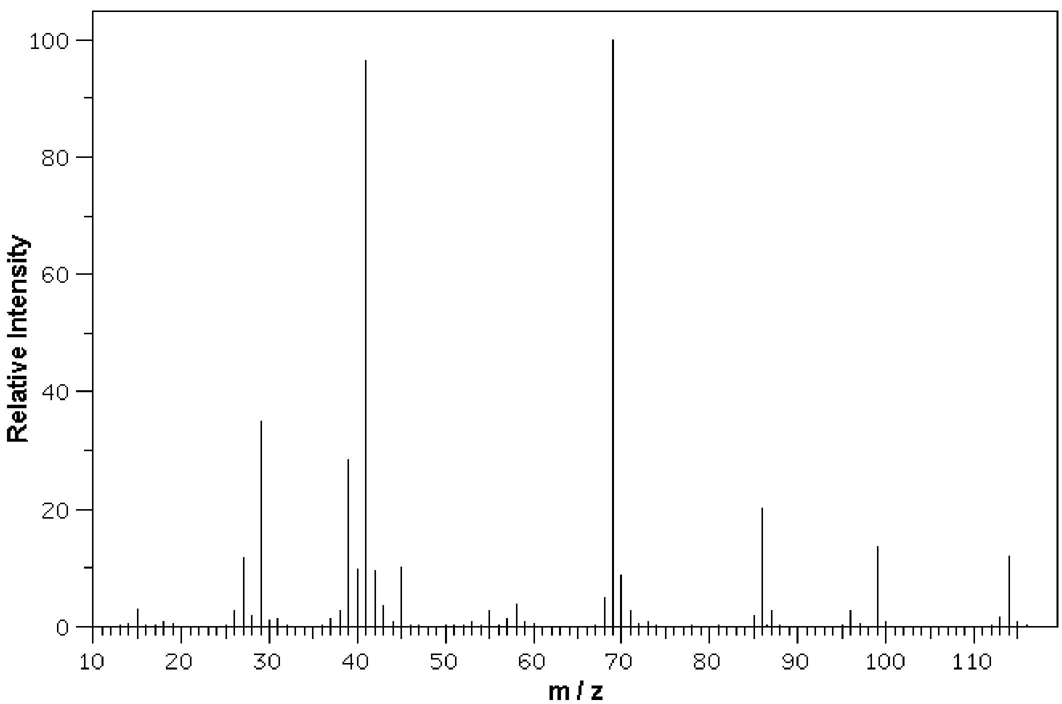
PART 9: SPECTROSCOPY

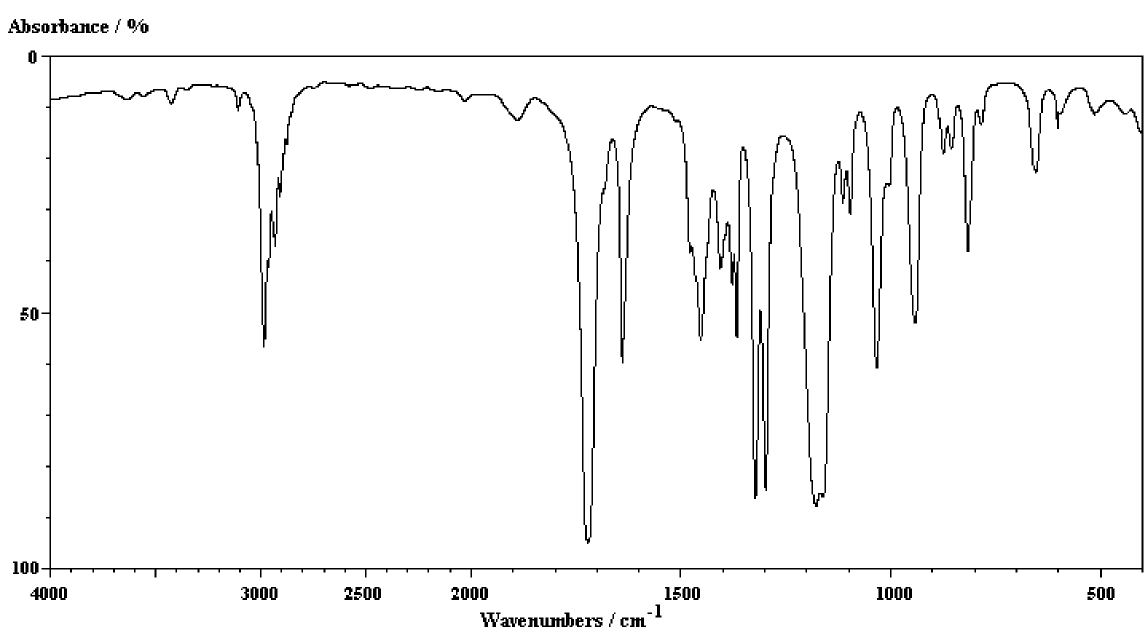
10% **WRITE YOUR ANSWERS IN THE BOOKLET PROVIDED**

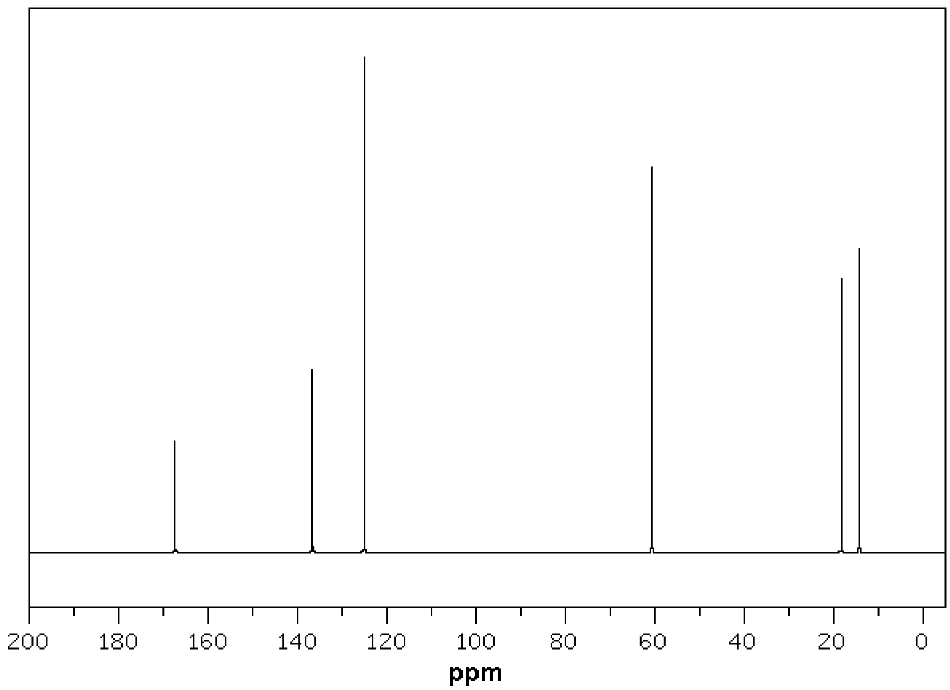
Show your working as PARTIAL marks will be given.

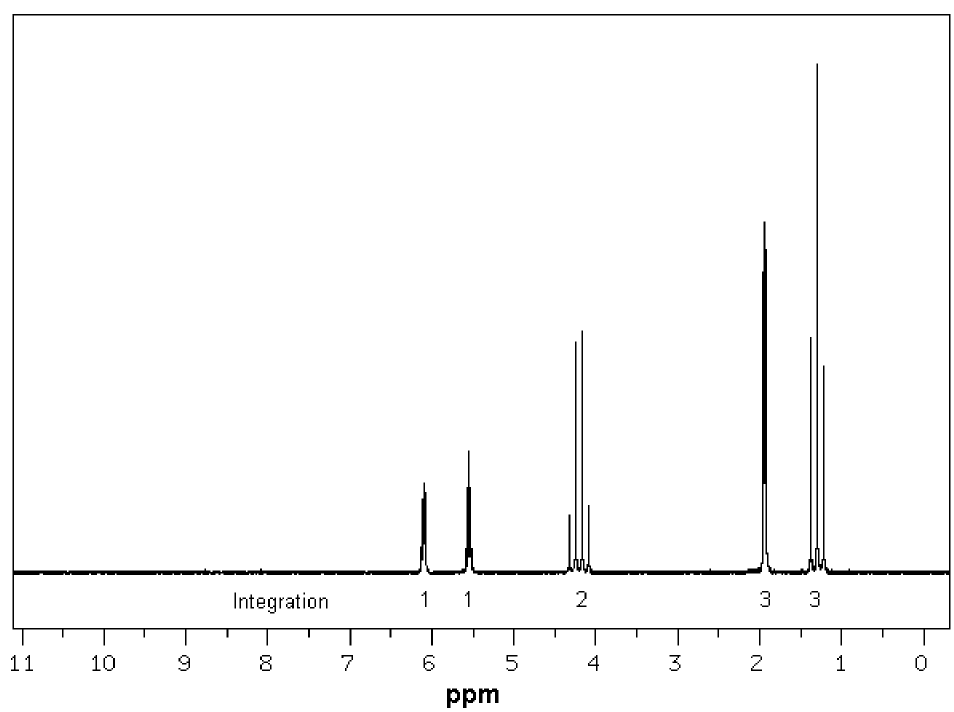
From the data provided below, identify the structure of the "unknown" molecule.

C, H elemental analysis : 63.14% C, 8.83% H






200
180
160
140
120
100
80
60
40
20
0
ppm


Integration
1
1
2
3
3
11
10
9
8
7
6
5
4
3
2
1
0
ppm

****** THE END ******