THE UNIVERSITY OF CALGARY

FACULTY OF SCIENCE

FINAL EXAMINATION

CHEMISTRY 351

December 13th, 2003

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 - 38, 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***.

20% PART 1 RELATIVE PROPERTIES

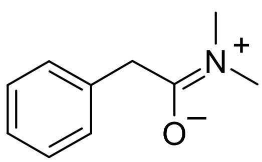
ANSWER ANY TEN (10) OF QUESTIONS 1 TO 14.

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

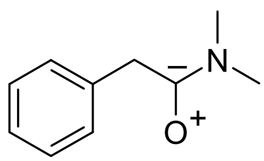
Use the following code to indicate your answers.

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

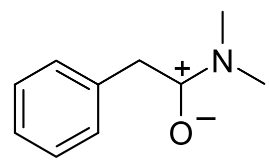
1. The relative importance of the following resonance contributors :



i

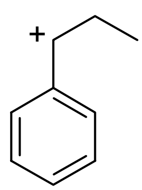


ii

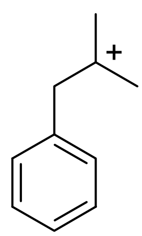


iii

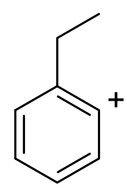
2. The relative stability of the following carbocations :



i

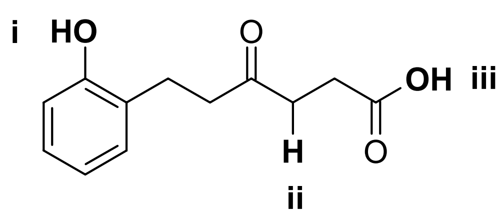


ii



iii

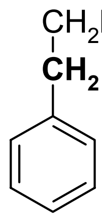
3. The pKa's of the bold **H** atoms indicated in the following structure:



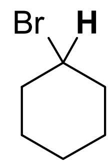
Use the following code to indicate your answers.

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

4. The number of peaks seen in the 1H NMR spectra coupling pattern corresponding to the group indicated in bold in each of the following:



i

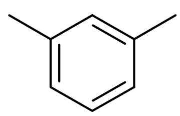


ii

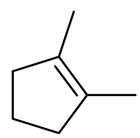
$CH_3-\mathbf{CH_2}-CH_2CH_3$

iii

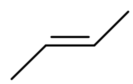
5. The number of peaks seen in the normal broadband proton decoupled 13C NMR spectrum for each of the following:



i



ii

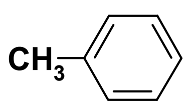


iii

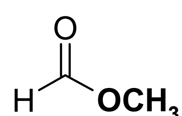
6. The [1]H-nmr chemical shifts for the groups shown in **bold** in each of the following structures :

$\mathbf{CH_3}-Br$

i



ii



iii

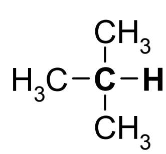
7. The relative strengths of the indicated bonds in each of the following:

Br—Br

i

H—**C**H_3

ii

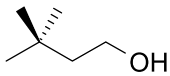


iii

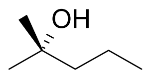
Use the following code to indicate your answers.

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

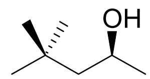
8. The relative rates of reaction of each of the following with conc. H_2SO_4 / heat:



i

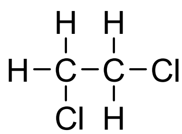


ii

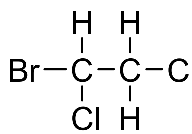


iii

9. The number of staggered conformations of different energies of each of the following :



i



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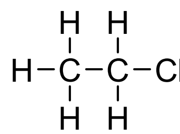
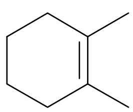
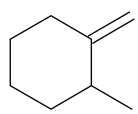


iii

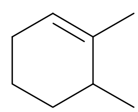
10. The heats of combustion, ΔH_c^o, of each of the following (least exothermic to most exothermic) :



i



ii



iii

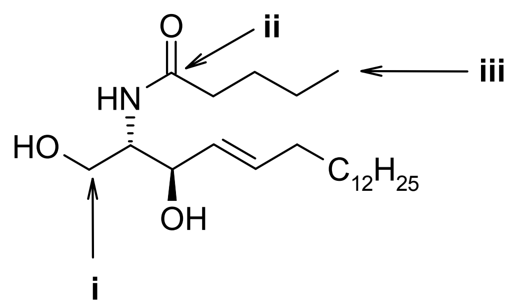
11. The number of possible alkene isomers that could be produced by the reaction of each of the following by heating with ethanolic KOH :

i 2-chloro-2-methylbutane
ii 1-chlorobutane
iii 2-chlorobutane

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**

12. The oxidation states of the **C atoms** indicated in the following structure:



13. The number of units of unsaturation (also known as the index of hydrogen deficiency or IHD) of each of the following molecular formulae:

$C_{10}H_{19}OCl$	$C_{11}H_{15}NO$	$C_9H_{12}O$
i	**ii**	**iii**

14. The ability of the group in **bold** to function as a leaving group in each of the following:

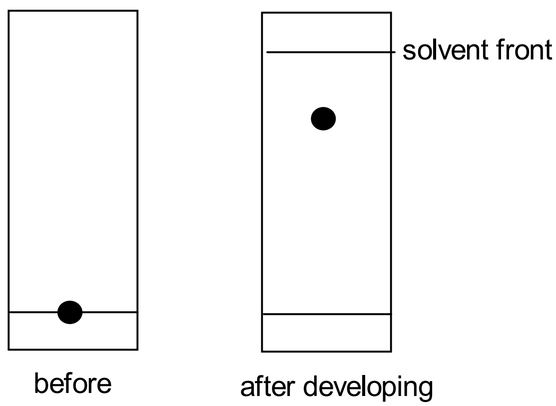
CH_3CH_2—**OTs**	CH_3CH_2—**Cl**	CH_3CH_2—**OH**
i	**ii**	**iii**

10% PART 2: LABORATORY

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. What is the Rf value for the sample spot shown on the chromatographic plate after development based on the sketch of the plate on the right in the figure below ?



A 1.20

B 0.75

C 0.67

D 0.5

E 0.25

16. Which of the following statements from the experiment "Reactivity in Substitution Reactions" using silver nitrate in aqueous ethanol are true ?

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

B silver halides are soluble in aqueous ethanol.

C this reaction indicates SN1 reactivity.

D chlorides are more reactive than bromides.

E t-butyl bromide reacted more rapidly than n-butyl bromide.

17. In the experiment about the reaction of bromine with hydrocarbons which of the following statements are true ?

A bromine reacts with alkenes to give 1,2-dibromides.

B bromine reacts with methylbenzene to give p-bromomethylbenzene.

C *iso*-propylbenzene reacts more rapidly than methylbenzene.

D t-butyl bromide reacts very slowly because it lacks a benzylic hydrogen.

E alkyl bromides are typically colourless.

18. Which of the following statements from the experiment "Reactivity in Substitution Reactions" using sodium iodide in acetone are true ?

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

    B sodium iodide is insoluble in acetone.

    C sodium iodide / acetone indicates SN1 reactivity.

    D chlorides are more reactive than bromides.

    E t-butyl bromide reacted more rapidly than n-butyl bromide.

19. Which of the following statements about laboratory techniques are true ?

    A a separatory funnel can be used to separate miscible solutions.

    B magnesium sulfate can be used to dry organic solutions.

    C boiling points increase as atmospheric pressure increases.

    D rapid heating will ensure efficient distillation.

    E a Buchner funnel should be used with a fluted filter paper.

Cont'd **-->**

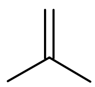
14% PART 3: REACTIONS

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

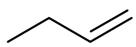
For each of questions 20-27 select either the major product or the starting material required in order to complete each of the reaction schemes

20.

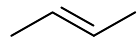
$(CH_3)_3CH$ $\xrightarrow[\text{2. } NaOCH_2CH_3\text{ / }CH_3CH_2OH\text{ / heat}]{\text{1. } Br_2\text{ / uv light}}$?



A



B



C

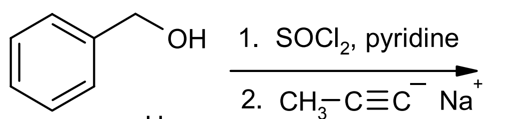
$(CH_3)_3COH$

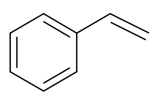
D

$(CH_3)_3COCH_2CH_3$

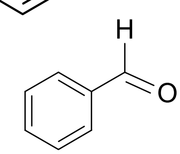
E

21.

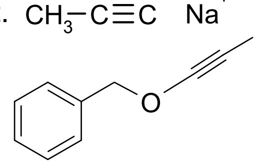




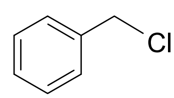
A



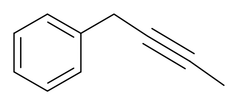
B



C

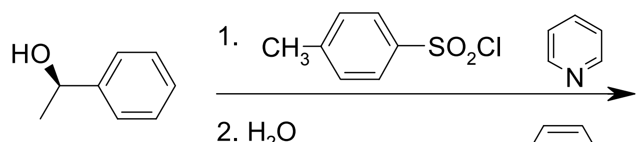


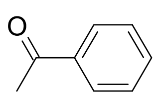
D



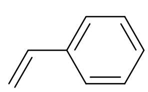
E

22.

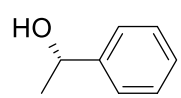




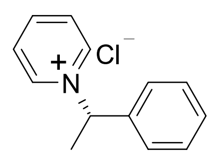
A



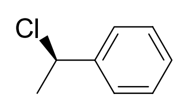
B



C

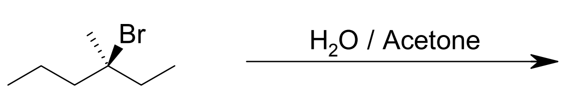


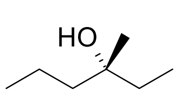
D



E

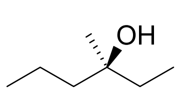
23.





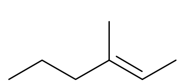
only

A

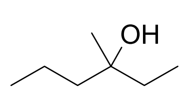


only

B

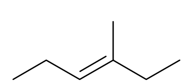


C



racemic

D



E

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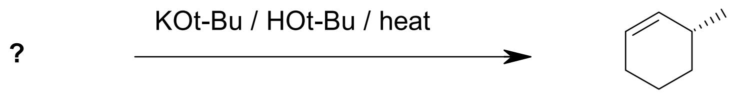
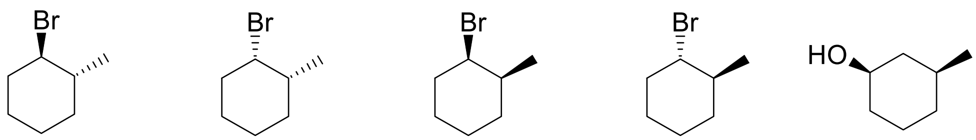
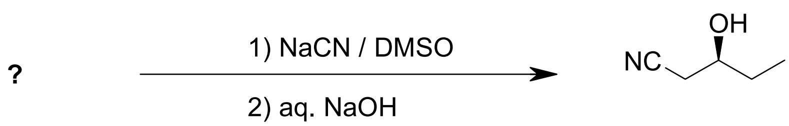
24.

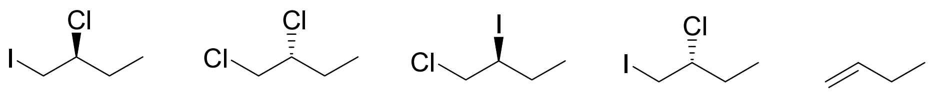




A **B** **C** **D** **E**

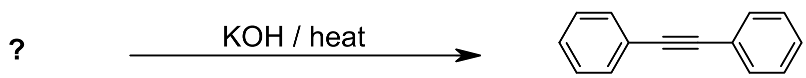
25.

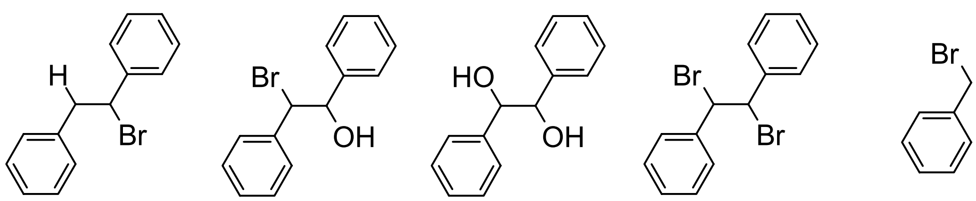




A **B** **C** **D** **E**

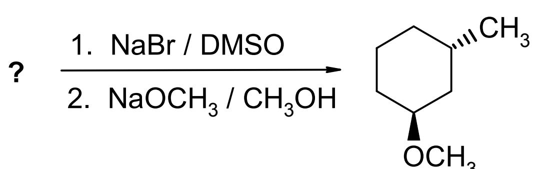
26.

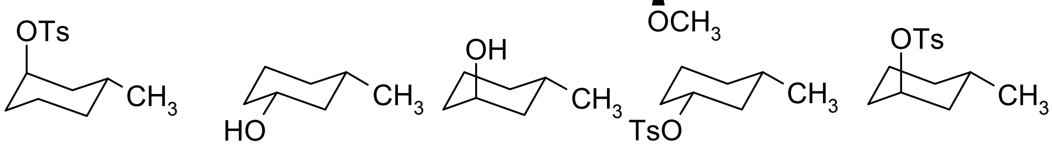




A **B** **C** **D** **E**

27.





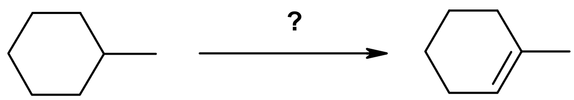
A **B** **C** **D** **E**

10% PART 4: REAGENTS FOR REACTIONS

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 conc. H_2SO_4 / heat

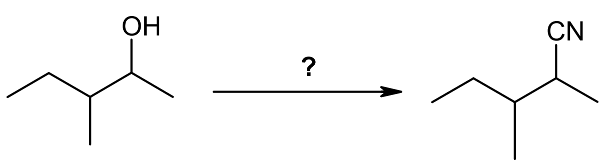
B KOH / EtOH / heat

C KOtBu / DMSO / heat

D 1. Br_2 / uv light
2. KOH / EtOH / heat

E 1. Cl_2 / uv light
2. KOH / EtOH / heat

29.



A HCN

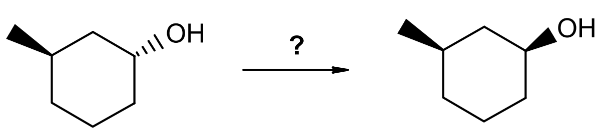
B NH_3

C KCN / DMSO

D 1. HBr
2. KCN / DMSO

E 1. TsCl / Et_3N
2. KCN / DMSO

30.



A H_2SO_4 / heat

B NaOH

C 1. $SOCl_2$ / Et_3N
2. aq. NaOH

D 1. Tosyl chloride, Et_3N
2. aq. NaOH

E H_2O / heat

31.

$$CH_3CH_2OH \xrightarrow{?} CH_3CH_2{-}O{-}C(CH_3)_3$$

A $(CH_3)_3COH$ / H^+

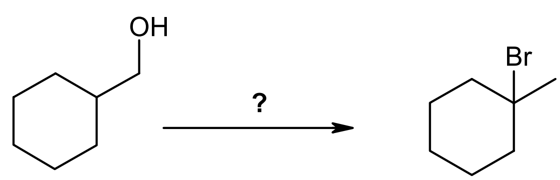
B Br_2

C CH_3Br

D 1. Na
2. $(CH_3)_3CBr$

E 1. Na
2. CH_3Br

32.



A Br_2 / heat

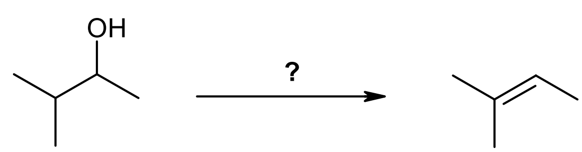
B HBr

C PBr_3 / Et_3N

D KBr / DMSO

E NaBr

33.



A HCl / heat

B KOH / heat

C NaOEt / EtOH / heat

D H_2SO_4 / heat

E Na

8% PART 5: SPECTROSCOPY

ANSWER ANY FOUR (4) OF QUESTIONS 34 - 38.

For ANY FOUR (4) of questions 34-38 select the compound from the list provided that corresponds BEST with the spectroscopic data provided.

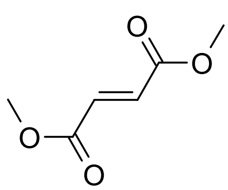
34. **^{1}H NMR** : δ 3.7 ppm (singlet, 6 H), 7.0 ppm (singlet, 2 H).

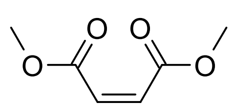
35. **^{1}H NMR** : δ 1.0 ppm (triplet, 3 H), 1.6 ppm (sextet, 2 H), 2.0 ppm (singlet, 3 H), 4.1 ppm (triplet, 2 H).
IR = 1745 cm^{-1}

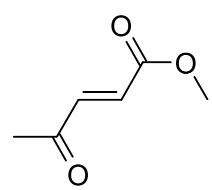
36. **^{1}H NMR** : δ1.0 ppm (triplet, 3 H), 1.5 ppm (sextet, 2 H), 3.4 ppm (triplet, 2 H).

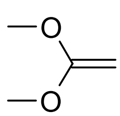
37. **^{1}H NMR** : δ2.3 ppm (singlet, 3 H), 3.8 ppm (singlet, 3 H), 6.9 ppm (doublet, *J*=16 Hz, 1 H), 7.3 ppm (doublet, *J* = 16 Hz, 1 H).
IR = 1725, 1675 and 1645 cm^{-1}

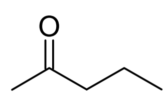
38. **^{1}H NMR** : δ 0.9 ppm (triplet, 3H) 1.6 ppm (sextet, 2 H), 2.3ppm (broad singlet, exchangeable, 1H), 3.6 ppm (triplet, 2H)
IR = ~ 3400 cm^{-1} (broad)

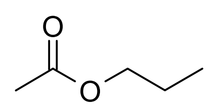
A 

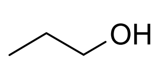
B 

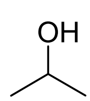
C 

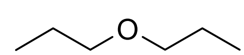
D 

E 

AB 

AC 

AD 

AE 

9% **PART 6: SYNTHESIS**

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

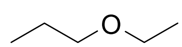
WRITE YOUR ANSWERS IN THE BOOKLET PROVIDED.

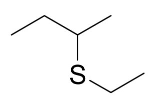
DO NOT SHOW MECHANISMS.

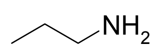
TARGETS

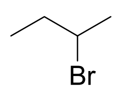
trans-2-butene

2-propanol

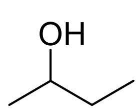


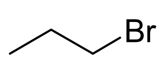






Allowed Starting Materials:





any compound with 2 or less C atoms

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

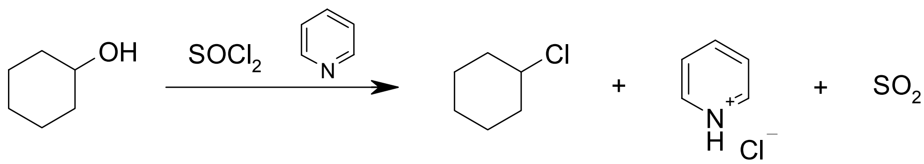
9% **PART 7: MECHANISMS**

WRITE YOUR ANSWERS IN THE BOOKLET PROVIDED

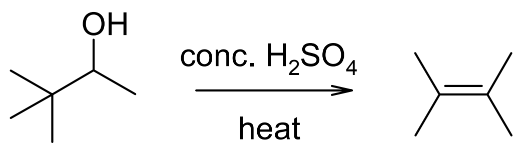
ANSWER ANY THREE (3) OF THE QUESTIONS I to IV.

Draw curly arrow mechanisms to explain any three (3) of the following reactions / observations. No other reagents are required.

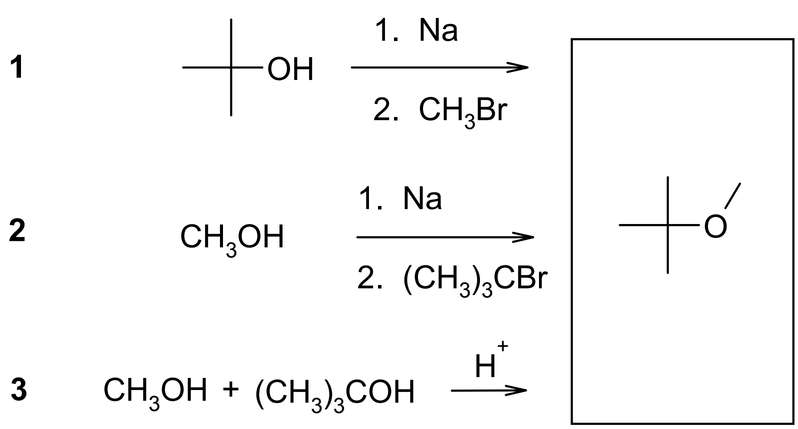
I.



II



III. Of the 3 ways shown below to make t-butyl methyl ether (as known as MTBE), a fuel additive, which method is most efficient and why ?



IV. Why does the halogen get introduced at different positions in the following reactions ?

$$(CH_3)_2CHCH_2Cl \xleftarrow[\text{heat}]{Cl_2} (CH_3)_3CH \xrightarrow[\text{heat}]{Br_2} (CH_3)_3CBr$$

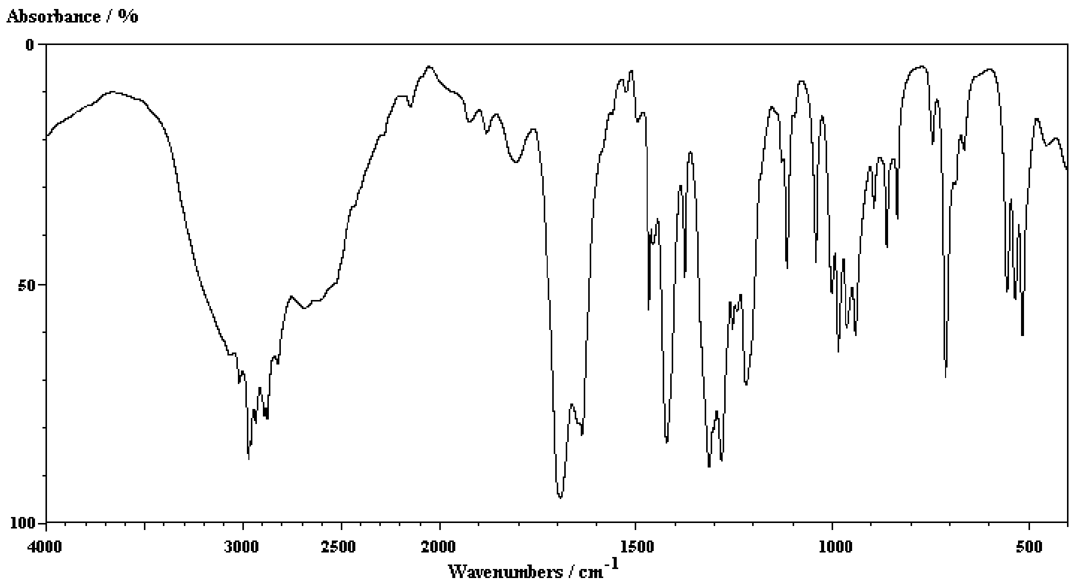
10% **PART 8: SPECTROSCOPY**

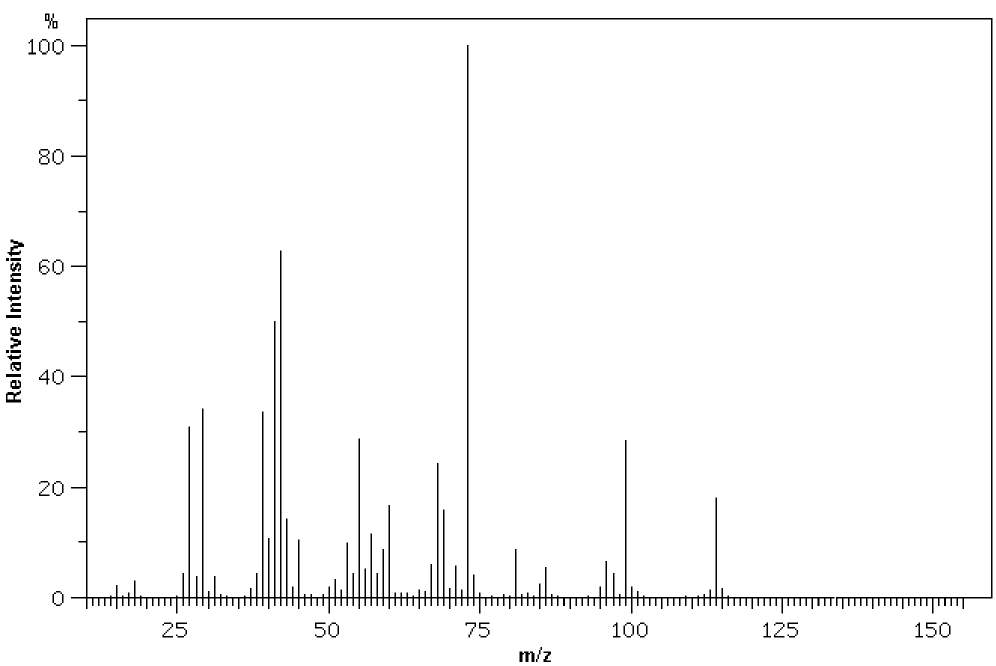
WRITE YOUR ANSWERS IN THE BOOKLET PROVIDED

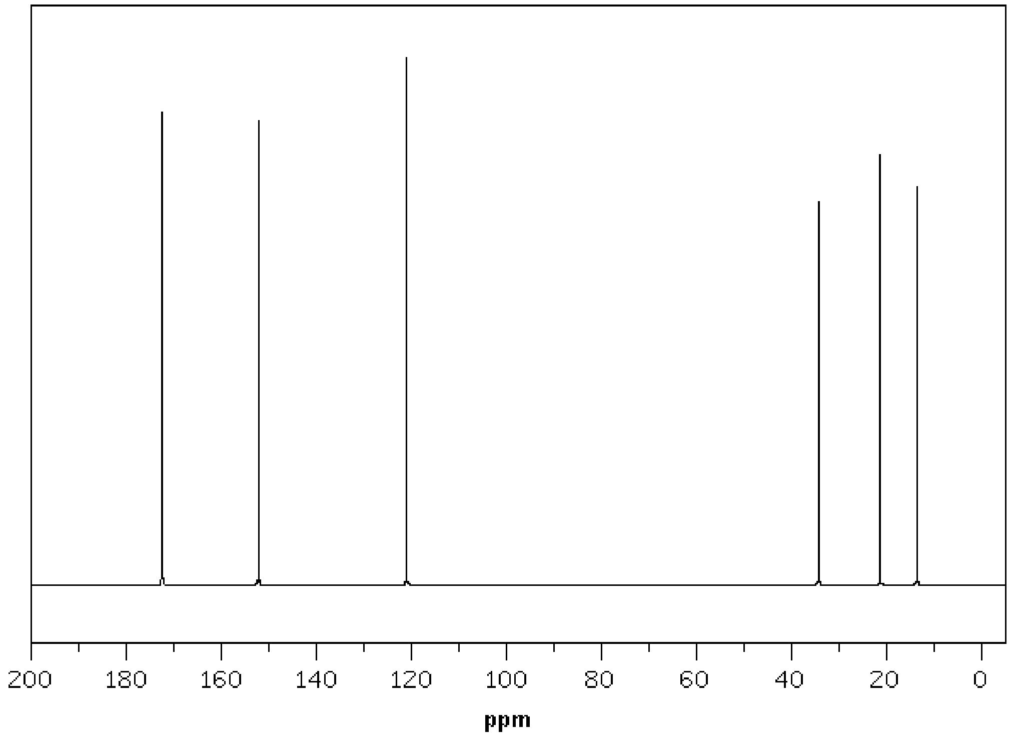
Show your workings as PARTIAL marks will be given.

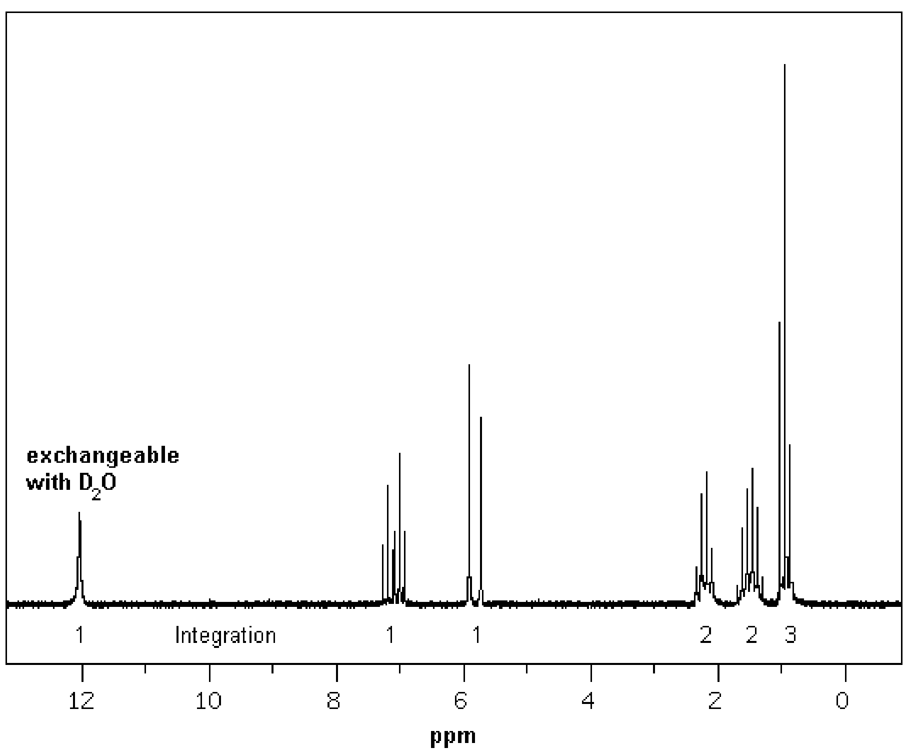
From the data provided below, identify the structure of the "unknown" molecule.

Elemental analysis for C and H only found : 63.14 %C and 8.83 %H






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


exchangeable with D_2O
1
Integration
1
1
2
2
3
12
10
8
6
4
2
0
ppm

Cont'd -->

10% PART 9: STRUCTURE DETERMINATION

WRITE YOUR ANSWERS IN THE BOOKLET PROVIDED

An alkyl bromide **A**, $C_5H_{11}Br$, was reacted with sodium hydroxide solution to give **B** $C_5H_{12}O$ (IR : 3500cm^{-1}, broad) as the major product.
Reaction of **B** with HBr gave **C** a constitutional isomer of **A**. When **C** was heated with KOtBu / t-butanol, the major product was **D**, C_5H_{10} (IR : 1650cm^{-1}). Whereas when **B** was reacted with PBr_3 / Et_3N, **A** was obtained. **C** could also be obtained on reaction of 2-methylbutane with bromine / uv light.
When **B** was heated with conc. H_2SO_4, the major product was **E**, a constitutional isomer of **D**. It was later found that **E** could also be prepared directly from **A** by reacting it with hot conc. KOH in ethanol.
In contrast, reaction of **A** with KOtBu / t-butanol/ heat gave **F**, which was a constitutional isomer of both **D** and **E**.
Reduction of **D**, **E**, and **F** using catalytic hydrogenation (H_2 / Pd) all gave the same alkane.
In a ^{13}C nmr spectroscopic analysis of the compounds, **A**, **B**, **C** and **F** each had 4 peaks, while **D** and **E** each had 5 peaks.
Of the compunds **A-F**, only **A** and **B** exist as pairs of enantiomers.

- **Identify A-F (only structures are needed)**
- **Give the complete name of one enantiomer of A**

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