THE UNIVERSITY OF CALGARY

FACULTY OF SCIENCE

FINAL EXAMINATION

CHEMISTRY 351

December 10th, 2002 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

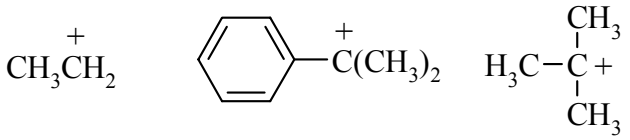
ANSWER ANY TEN (10) OF QUESTIONS 1 TO 14.

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.

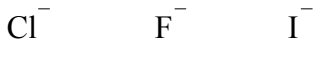
A.	**i > ii > iii**	**D**.	**ii > iii > i**
B.	**i > iii > ii**	**E**.	**iii > i > ii**
C.	**ii > i > iii**	**AB**.	**iii > ii > i**

1. The relative stability of the following carbocations:



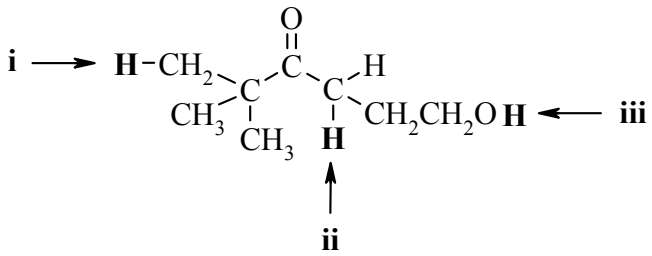
i **ii** **iii**

2. The relative nucleophilicity of the following anions in aqueous solution:

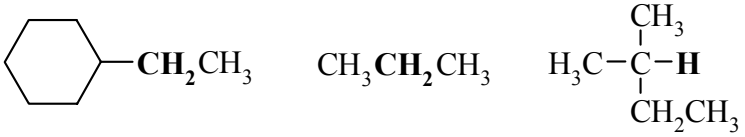


i **ii** **iii**

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



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:

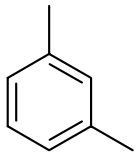


i **ii** **iii**

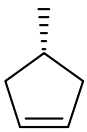
Use the following code to indicate your answers.

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

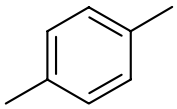
5. The number of peaks seen in the normal broadband proton decoupled 13C NMR spectrum for each of the following:



i

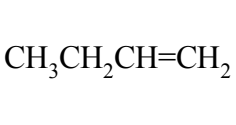


ii

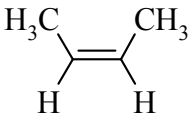


iii

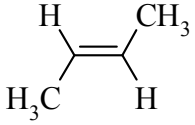
6. The heats of combustion of each of the following (least exothermic to most exothermic) :



i



ii

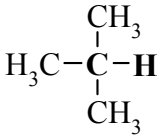


iii

7. The relative strengths of the indicated **H-X** bonds in each of the following:

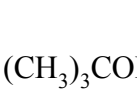
i

ii

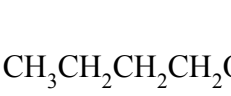


iii

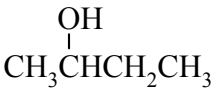
8. The relative rates of reaction of each of the following with conc. H_2SO_4 / heat:



i



ii

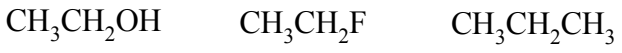


iii

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**

9. The boiling points (at 1 atmosphere pressure) of each of the following :



i **ii** **iii**

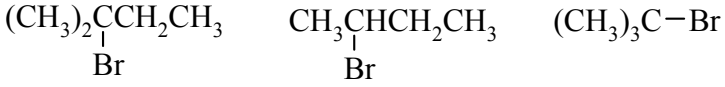
10. The heats of formation, ΔH_f^o, of each of the following (least exothermic to most exothermic) :

i cis-1,2-dimethylcyclohexane

ii trans-1,4-dimethylcyclohexane

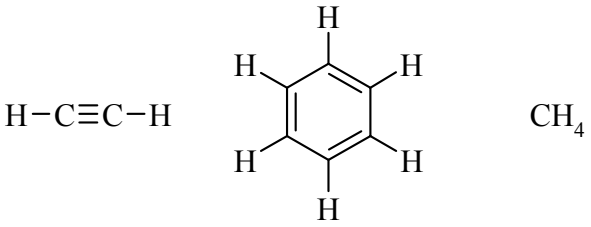
iii trans-1,2-dimethylcyclohexane

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



i **ii** **iii**

12. The bond stretching frequencies /cm^{-1} in the infra-red spectra for the C-H bonds in each of the following :



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 number of units of unsaturation in each of the following molecular formulae:

$C_7H_4O_2Cl_2$	$C_7H_{10}N_2$	$C_6H_{11}N_3O_2$
i	**ii**	**iii**

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

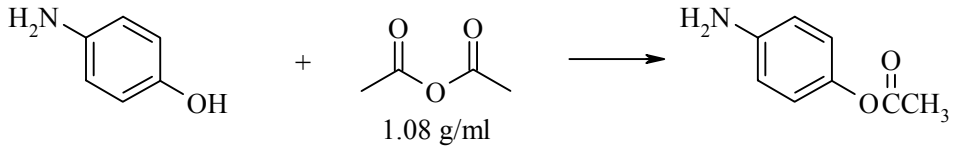
CH_3CH_2—**OTs**	CH_3CH_2—**F**	CH_3CH_2—**Br**
i	**ii**	**iii**

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. 1.09g of p-aminophenol was reacted with 1.12g of acetic anhydride, and 0.906g of acetaminophen was obtained. What % yield of acetaminophen was obtained ?



A 92 % **B** 81 % **C** 72 % **D** 60 % **E** 55 %

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

A the Lucas test ($HCl / ZnCl_2$) is an example of an SN1 reaction.

B the tertiary alcohols were oxidised to ketones.

C bromine was used to detect the presence of an alkene.

D the relative reactivity towards dehydration was $3^o > 2^o > 1^o$.

E the insoluble layer that forms in the Lucas test is the non-polar alkane.

17. In the experiment about the reactivity of alcohols, which of the following statements about the reagent 2,4-dinitrophenylhydrazine (2,4-DNP) are true ?

A it reacts with the alcohol giving a precipitate.

B 2,4-DNP is used as a colourless solution.

C if a carboxylic acid is presented, a yellow precipitate is formed.

D if an aldehyde or ketone is formed a yellow to red precipitate is formed.

E 2,4-DNP oxidises alcohols to carbonyl compounds.

18. Which of the following statements about the experiment "Reactivity in Substitution Reactions" are true ?

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

B sodium chloride is insoluble in acetone.

C sodium iodide / acetone gives SN1 reactivity

D crotyl chloride is 1-chloro-2-butene.

E the precipitates that form are the halide salts.

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

A boiling points are higher at sea-level than at higher altitude.

B a fractionating column should have a steady flow of water to cool it.

C a Büchner funnel is used for vacuum filtrations.

D charcoal can be used to remove water from organic solutions.

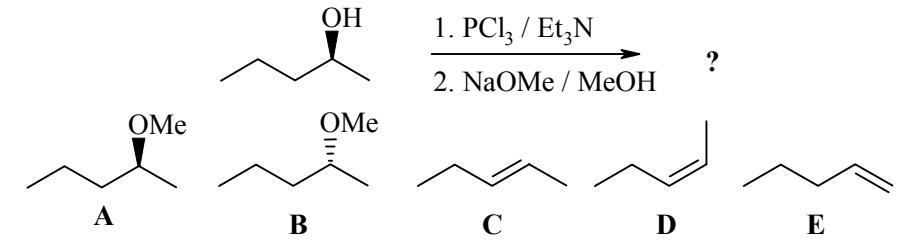
E a separatory funnel could be used to separate miscible liquids.

14% **PART 3: REACTIONS**

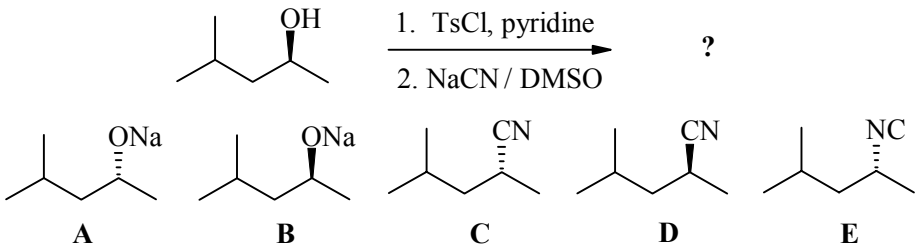
ANSWER ANY SEVEN (7) OF QUESTIONS 20-27.

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

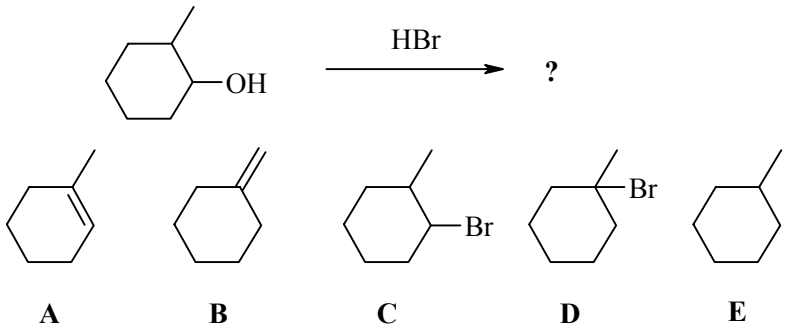
20.



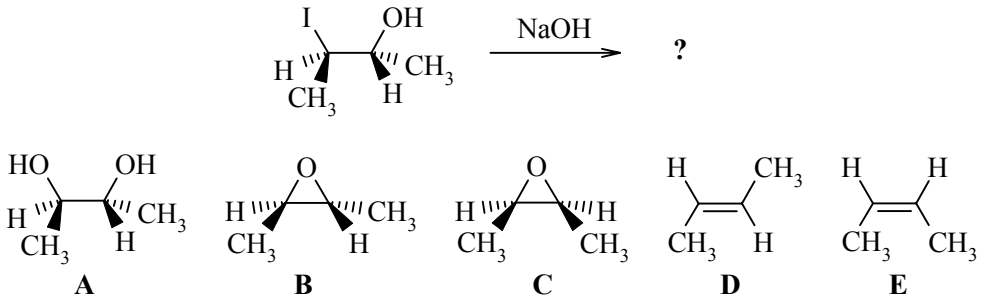
21.



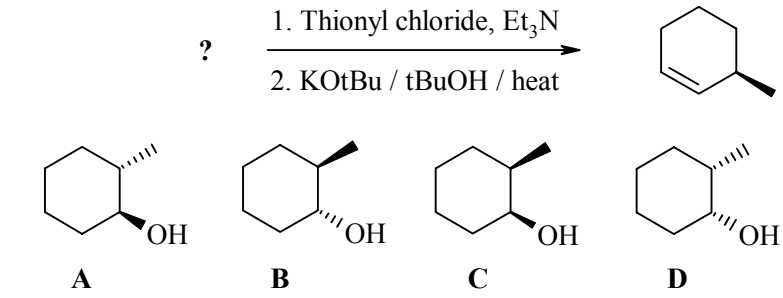
22.



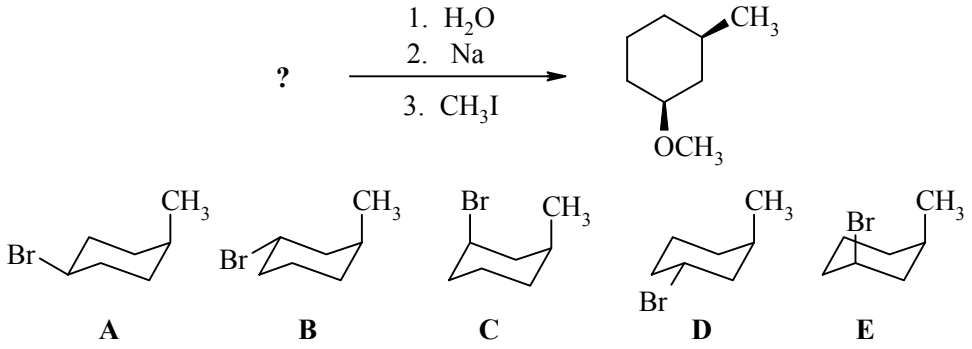
23.



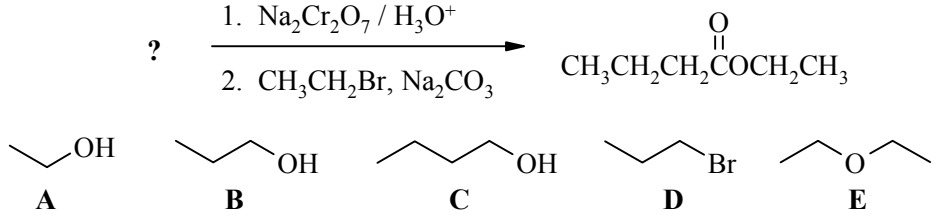
24.


?
1. Thionyl chloride, Et3N
2. KOtBu / tBuOH / heat
OH
OH
OH
OH
A
B
C
D
E

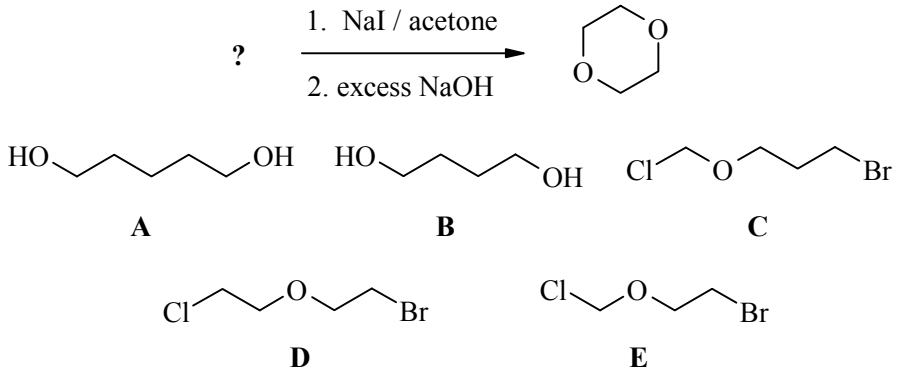
25.


?
1. H2O
2. Na
3. CH3I
CH3
OCH3
CH3
Br
CH3
Br
Br
CH3
CH3
Br
CH3
Br
A
B
C
D
E

26.


?
1. Na2Cr2O7 / H3O+
2. CH3CH2Br, Na2CO3
O
CH3CH2CH2COCH2CH3
OH
OH
OH
Br
O
A
B
C
D
E

27.

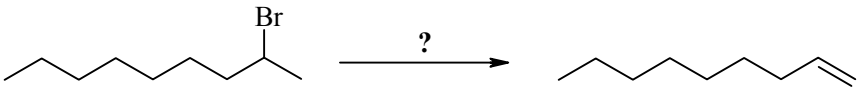

?
1. NaI / acetone
2. excess NaOH
O
O
HO
OH
HO
OH
Cl
O
Br
Cl
O
Br
Cl
O
Br
A
B
C
D
E

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

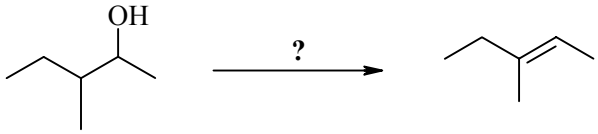
B KOH / EtOH / heat

C KOtBu / DMSO / heat

D 1. TsCl / Et_3N
2. KOH / EtOH / heat

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

29.



A conc. H_2SO_4 / heat

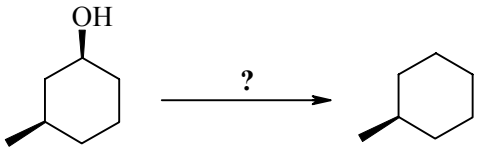
B KOH / EtOH / heat

C KOtBu / DMSO / heat

D 1. TsCl / Et_3N
2. KOH / EtOH / heat

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

30.



A H_2SO_4 / heat

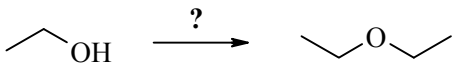
B NaOH

C 1. NaOH / heat
2. H_2 / catalyst

D 1. H_2SO_4 / heat
2. H_2 / catalyst

E 1. H_2 / catalyst
2. H_2SO_4 / heat

31.



A NaOH

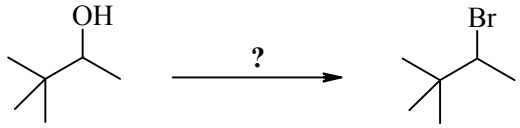
B Br_2

C CH_3Br

D 1. Na
2. CH_3CH_2Br

E 1. Na
2. CH_3Br

32.



A Br_2 / heat

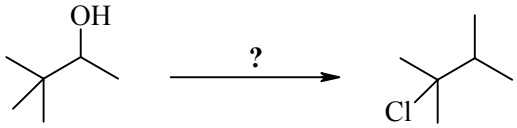
B HBr

C PBr_3 / Et_3N

D KBr / DMSO

E NaBr / H_2SO_4

33.



A Cl_2 / heat

B HCl

C PCl_3 / Et_3N

D NaCl / DMSO

E $SOCl_2$ / Et_3N

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 3.3ppm (singlet, 3H), 3.7ppm (singlet, 1H)

35. ^{1}H NMR : δ 3.3ppm (singlet, 3H), 3.7ppm (singlet, 2H)

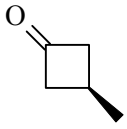
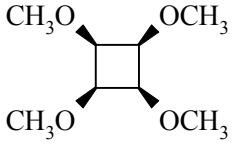
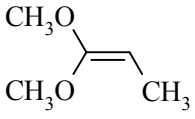
36. ^{1}H NMR : δ 2.1ppm (singlet, 3H), 2.4ppm (singlet, 2H)
IR : 1700 cm^{-1}

37. ^{1}H NMR : δ 1.0ppm (doublet, 3H) 3.3ppm (singlet, 6H), 4.5ppm (quartet, 1H)

38. ^{1}H NMR : δ 1.0ppm (doublet, 6H) 1.8ppm (broad singlet, exchangeable, 1H), 3.7ppm (septet, 1H)
IR = ~ 3400 cm^{-1} (broad)

A $CH_3OCH_2CH_2OCH_3$ **B** $CH_3CH(OCH_3)_2$ **C** $HOCH(CH_3)_2$

D $CH_3CH_2CH_2OH$ **E** $CH_3CCH_2CH_2CCH_3$ (O, O) **AB** $CH_3OCCH_2CH_2OCCH_3$ (O, O)

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

1-methoxybutane

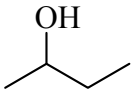
trans-2-butene

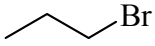
$(CH_3CH_2CH_2)_2O$

$CH_3CH_2CH_2CH_2CH_3$

$CH_3CH_2\underset{\displaystyle NH_2}{\underset{|}{C}}HCH_3$

Allowed Starting Materials:





any compound with 2 or less C atoms

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

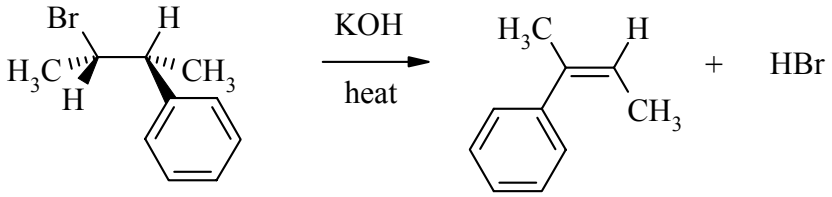
9% **PART 7: MECHANISMS**

WRITE YOUR ANSWERS IN THE BOOKLET PROVIDED

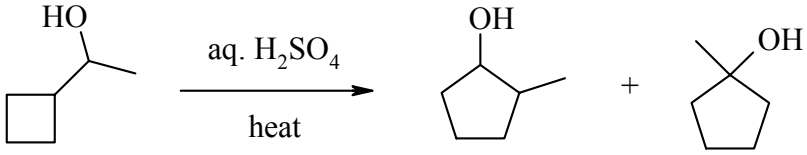
ANSWER ANY THREE (3) OF THE QUESTIONS I to IV.

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

I.



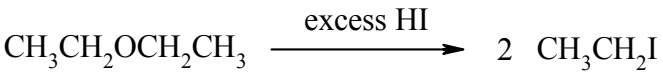
II



III. Predict which of the following is more reactive towards methyl iodide and indicate why.

1 **2**

IV. Alcohols and ethers react with hydroiodic acid via a similar mechanistic path. Using this similarity, draw the mechanism to account for the transformation shown below:



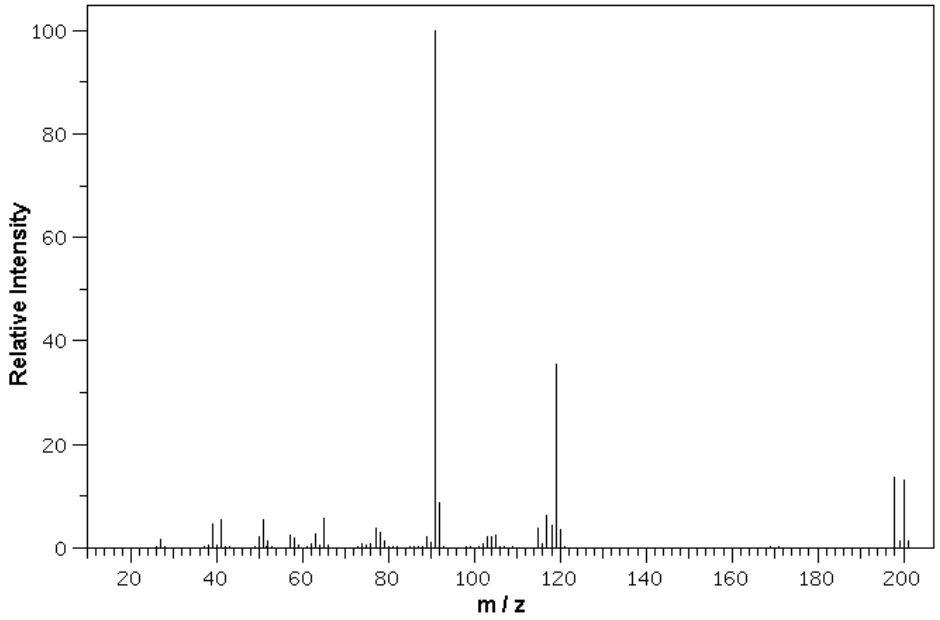
10% PART 8: SPECTROSCOPY

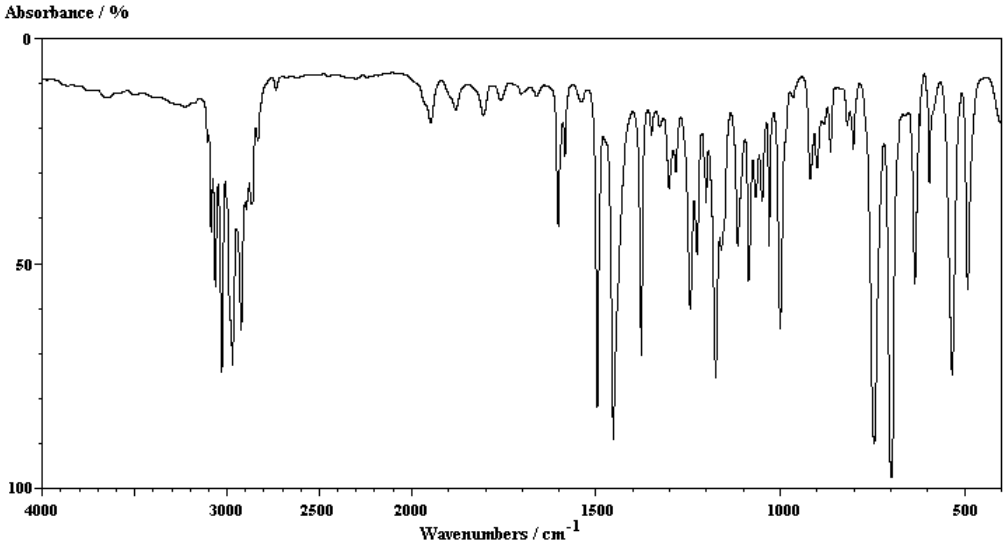
WRITE YOUR ANSWERS IN THE BOOKLET PROVIDED

Show your workings as PARTIAL marks will be given.

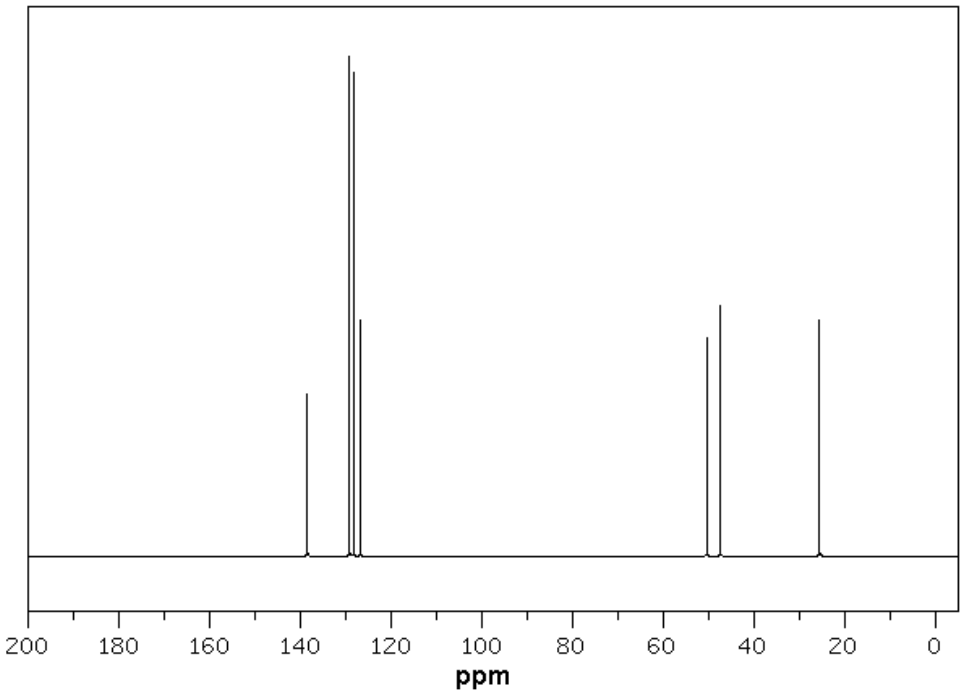
From the data provided below, identify the structure of the "unknown" molecule.

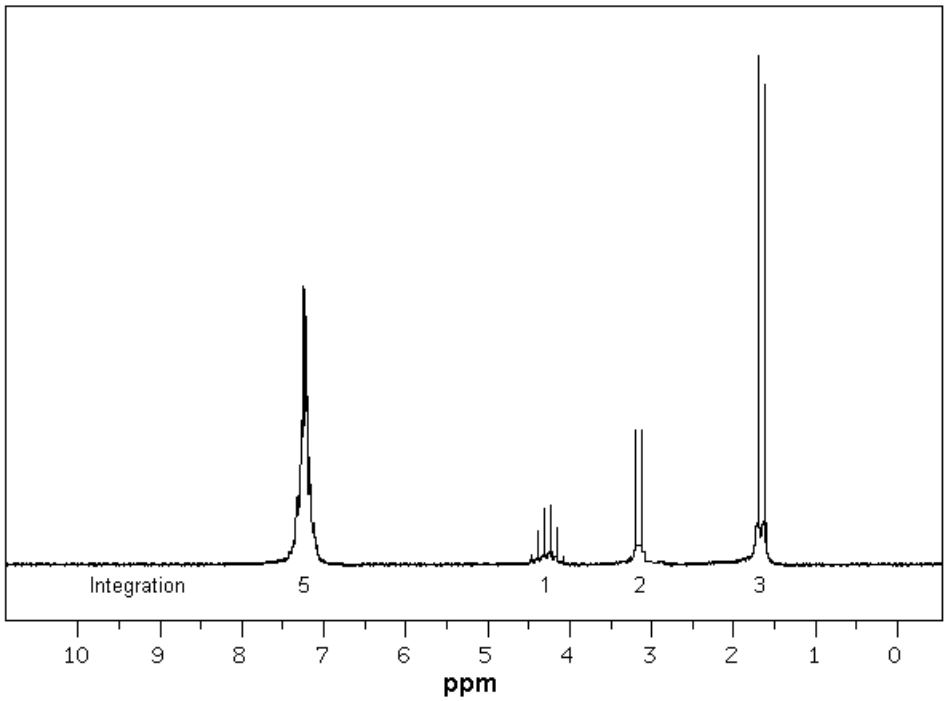
Elemental analysis for C,H, N found only: 54.30 %C and 5.57 %H





3087	57	2898	62	1302	66	1116	59	900	70
3064	46	2864	62	1285	70	1086	46	746	12
3029	27	1602	58	1245	41	1067	64	699	4
2989	38	1585	72	1226	62	1050	64	636	46
2970	28	1497	20	1202	64	1031	53	596	68
2950	58	1454	12	1176	26	1001	36	535	26
2924	36	1378	31	1162	63	920	68	492	44


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


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

10% PART 9: STRUCTURE DETERMINATION

WRITE YOUR ANSWERS IN THE BOOKLET PROVIDED

Compound **A**, C_6H_{10}, (IR absorption 1650cm^{-1}) was tested with Br_2 / $CHCl_3$ and gave a colourless solution. Careful reaction of **A** using Br_2 / uv light gave, **B**, C_6H_9Br that also reacted with Br_2 / $CHCl_3$ to give a colourless solution. **B** was found to react quickly with both NaI / acetone and $AgNO_3$ / aq. ethanol. When **B** was reacted with aq. NaOH at room temperature, it very rapidly gave **C**, $C_6H_{10}O$ (IR absorption 3400cm^{-1} (broad), 1650cm^{-1}). **C** was found to react rapidly with the Lucas reagent (HCl / $ZnCl_2$), and also with Br_2 / $CHCl_3$ to give a colourless solution.

Subsequent oxidation of **C** with a chromate reagent gave **D**, C_6H_8O (IR absorptions 1685cm^{-1}, 1615cm^{-1}). **D** gave a red-orange precipitate when tested with 2,4-dinitrophenylhydrazine (2,4-DNP). Reduction of **D** with H_2 / catalyst gave **E** an isomer of **C** (IR absorption 1715cm^{-1}). **E** also gave a red-orange precipitate when tested with 2,4-DNP.

Reduction of **C** with H_2 / catalyst gave **F**, $C_6H_{12}O$ (IR absorption 3500cm^{-1}) that was oxidised with a chromate reagent to again yield **E**.

Only **B** and **C** have chirality centers.

- **Identify the compounds A-F (you only need to draw the structures)**

- **Match the following ^{13}C nmr spectral data to the appropriate compound A-F:**

  I 200, 151, 130, 38, 25, 23 ppm

  II 127, 25, 23 ppm

- **Explain why B is the major product from the reaction of A with Br_2 / uv light**

**** THE END ****