THE UNIVERSITY OF CALGARY

FACULTY OF SCIENCE

FINAL EXAMINATION

CHEMISTRY 351

DECEMBER 15th 2000 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 is appended to the exam.

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

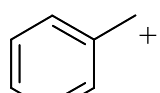
20% **ANSWER ANY TEN (10) OF QUESTIONS 1 TO 14.**

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

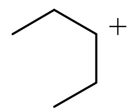
Use the following code to indicate your answers.

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)



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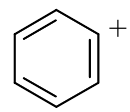
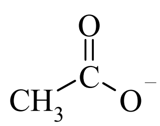
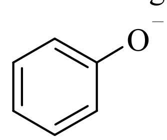


(iii)

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



(i)



(ii)

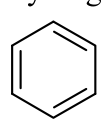
$CH_3CH_2O^-$

(iii)

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

CH_3CH_2OH	$(CH_3)_2NH$	CH_3CH_2SH
(i)	(ii)	(iii)

4. The index of hydrogen deficiency (IHD) of the following:



(i)

$C_8H_{13}OCl$

(ii)

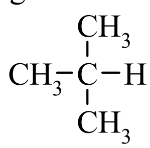
cyanocyclobutane

(iii)

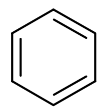
Use the following code to indicate your answers.

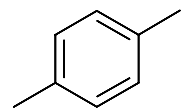
A.	**i** > **ii** > **iii**	**D.**	**ii** > **iii** > **i**
B.	**i** > **iii** > **ii**	**E.**	**iii** > **i** > **ii**
C.	**ii** > **i** > **iii**	**AB.**	**iii** > **ii** > **i**

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



(i)

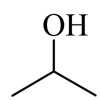

(ii)


(iii)

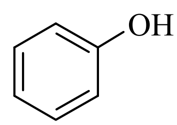
6. The relative rate of reaction of each of the following with HBr:

$(CH_3)_3COH$

(i)



(ii)



(iii)

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

$CH_3\mathbf{CH_3}$ (i)

$CH_3\mathbf{CH_2}Cl$ (ii)

Br
$CH_3\mathbf{CH}CH_3$ (iii)

8. The relative rates of reaction with NaF in DMSO of each of the following:

$(CH_3)_2CH-Cl$ (i)

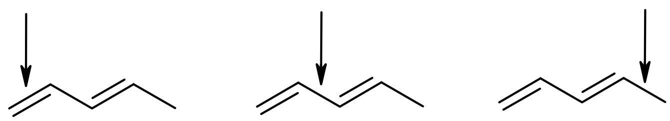
CH_3CH_2-Br (ii)

CH_3-OH (iii)

Use the following code to indicate your answers.

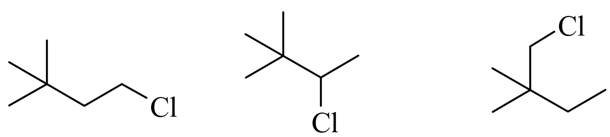
A.	**i > ii > iii**	**D.**	**ii > iii > i**
B.	**i > iii > ii**	**E.**	**iii > i > ii**
C.	**ii > i > iii**	**AB.**	**iii > ii > i**

9. The relative lengths of the indicated bonds in each of the following :



(i) (ii) (iii)

10. The relative yields of the following products from the reaction of 2,2-dimethylbutane with Cl_2 / UV light:



(i) (ii) (iii)

11. The relative yields of the Zaitsev product produced by the reaction of 2-bromo-2,3-dimethylbutane with each of the following:

$NaOCH_2CH_3$	$NaOCH_3$	$NaOC(CH_3)_3$
(i)	(ii)	(iii)

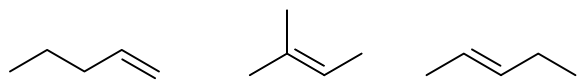
12. The boiling points of the following:

$CH_3(CH_2)_6OH$	$(CH_3)_3CC(CH_3)_3$	$CH_3(CH_2)_6CH_3$
(i)	(ii)	(iii)

Use the following code to indicate your answers.

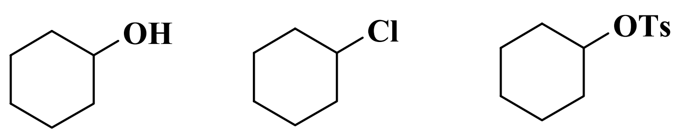
A.	**i** > **ii** > **iii**	**D**.	**ii** > **iii** > **i**
B.	**i** > **iii** > **ii**	**E**.	**iii** > **i** > **ii**
C.	**ii** > **i** > **iii**	**AB**.	**iii** > **ii** > **i**

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

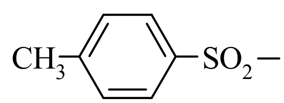


(i) (ii) (iii)

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



(i) (ii) (iii)

nb. Ts- = tosylate = 

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. 1.09 g of p-aminophenol (mw = 109 g/mol) was reacted with 1.12 g of acetic anhydride (mw = 102 g/mol), and a 75% yield of acetaminophen (mw = 151g/mol) was obtained. How many g of acetaminophen were obtained ?

A 1.51g

B 1.24g

C 1.13g

D 0.84g

E 0.82g

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 SN2 reaction.

B the secondary alcohols were oxidised to carboxylic acids.

C sulphuric acid was used as an oxidising agent.

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

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

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

A the bromine reacts with the alcohol.

B bromine in chloroform is a colourless solution.

C if an alkene is presented, a colourless dibromide is formed.

D the reaction of bromine with the alkene is an example of a substitution reaction.

E a white precipitate of NaBr forms.

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, aprotic solvent.

B sodium iodide is insoluble in acetone.

C this is an example of E2 reaction.

D the tertiary chloride reacted the fastest under these reaction conditions.

E chlorine is a better leaving group than bromine.

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 water reacts as a nucleophile, the product is an alcohol.

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

D the tertiary chloride reacted rapidly under these conditions.

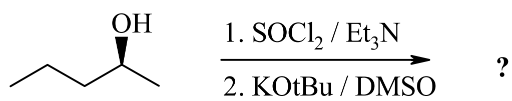
E the solvent is polar and favours the carbocation intermediate.

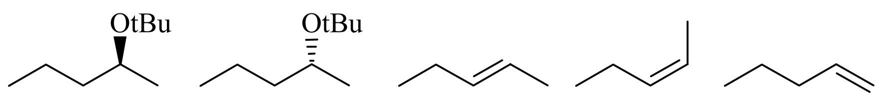
PART 3: REACTIONS

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

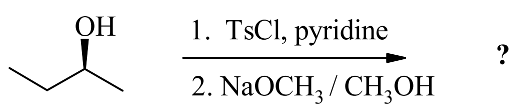
20.

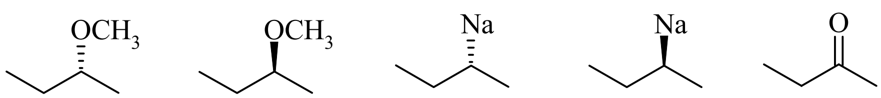




A B C D E

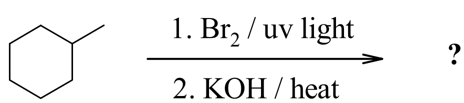
21.

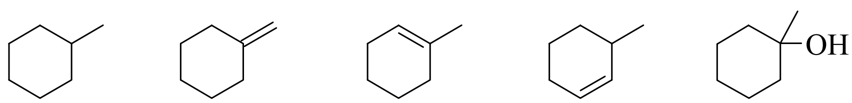




A B C D E

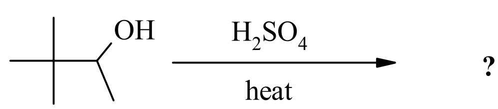
22.

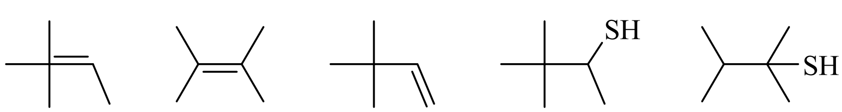




A B C D E

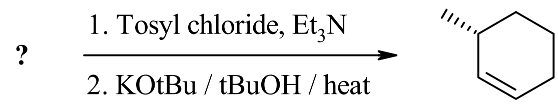
23.

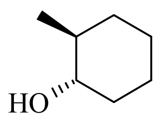




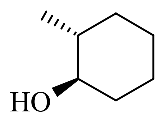
A B C D E

24.

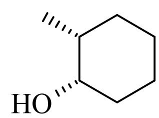




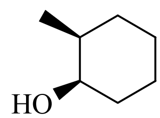
A



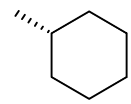
B



C

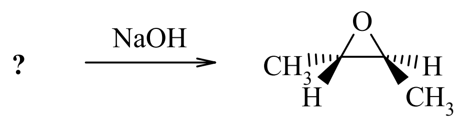


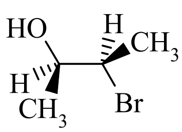
D



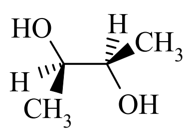
E

25.

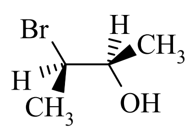




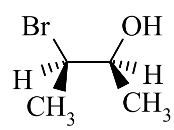
A



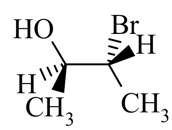
B



C

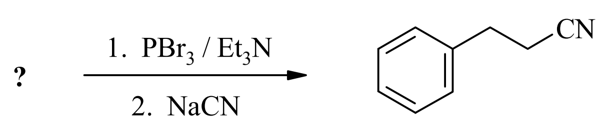


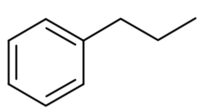
D



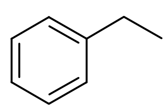
E

26.

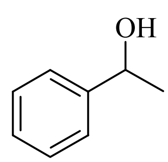




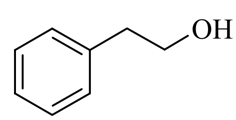
A



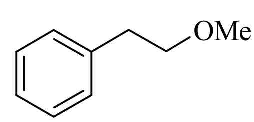
B



C

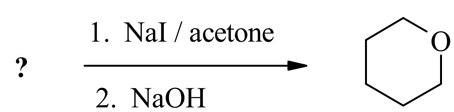


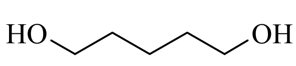
D



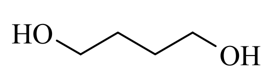
E

27.

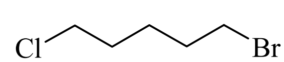




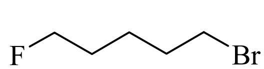
A



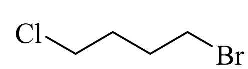
B



C



D



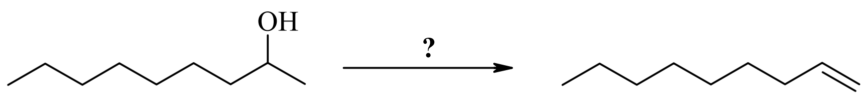
E

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 conc. H_2SO_4 / heat

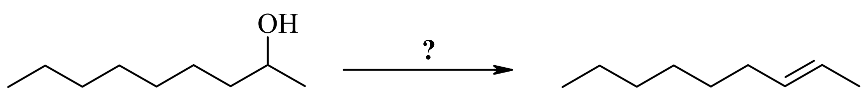
B KOH / EtOH / heat

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

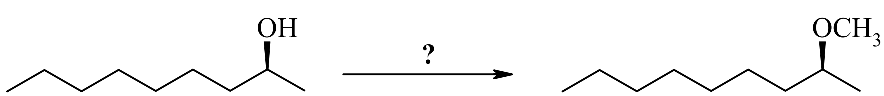
B KOH / EtOH / heat

C KOtBu / DMSO / heat

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

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

30.



A CH_3OCH_3

B CH_3OH / heat

C 1. Na 2. CH_3I

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

E $NaOCH_3$ / CH_3OH

31.

$$(CH_3)_3CH \xrightarrow{?} (CH_3)_2CHCH_2Br$$

A Br_2 / uv light

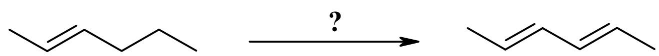
B HBr

C NaBr / DMSO

D 1. Cl_2 / uv light
2. NaBr / DMSO

E 1. PCl_3 / Et_3N
2. NaBr / DMSO

32.



A aq. H_2SO_4

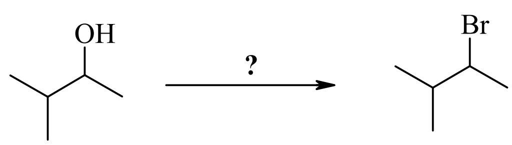
B conc. H_2SO_4

C KOH / heat

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

E 1. KOH / heat
2. NaBr / DMSO

33.



A Br_2 / uv light

B HBr

C PBr_3 / Et_3N

D NaBr / DMSO

E NaBr / H_2SO_4

PART 5: MECHANISMS

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

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

A	Walden	**AB**	carbanion	**BD**	leaving group
B	Williamson	**AC**	carbocation	**BE**	staggered
C	Zaitsev	**AD**	radical	**CD**	anti-periplanar
D	nucleophile	**AE**	stepwise	**CE**	steric effect
E	electrophile	**BC**	concerted	**DE**	homolytic

34. an intermediate in a nucleophilic substitution reaction

35. a reaction where all the bond changes occur simultaneously

36. the more highly substituted alkene product

37. a group that is displaced with the bonding electrons

38. the spatial requirement in an E2 reaction

39. why SN2 reactions are slow for 3^o substrates

40. a species with a single unpaired electron

41 the inversion in an SN2 reaction

42. formed during the rate determining step of an E1 reaction

43. a bond breaking process resulting in unpaired electrons

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

cyclohexene

ethoxycyclohexane

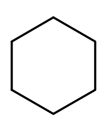
diethyl ether

$(CH_3)_3C-OH$

$CH_3\overset{\overset{CH_3}{|}}{C}HCH_2OH$

CH_3CH_2CN

Allowed Starting Materials:



CH_3CH_3

$CH_3\overset{\overset{CH_3}{|}}{C}HCH_3$

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

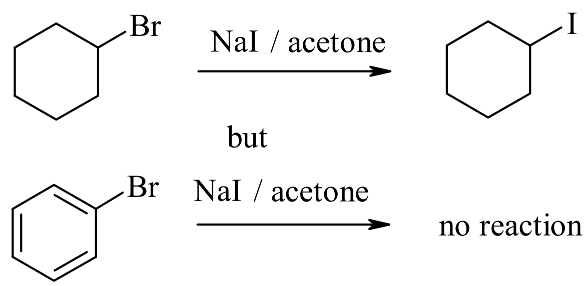
PART 7: MECHANISMS

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

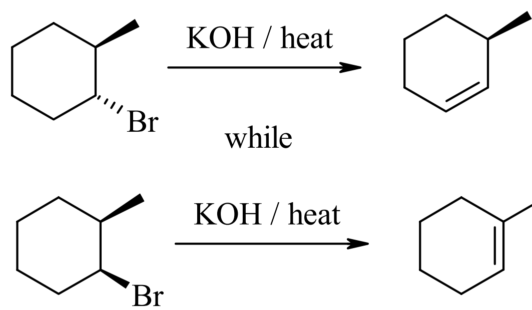
ANSWER ANY THREE (3) OF THE QUESTIONS I to IV.

Using curly arrow mechanisms, explain the following observations:

I.



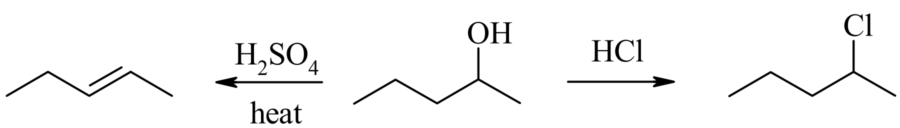
II.



III.

$$CH_3CH_3 \xrightarrow{Br_2\ /\ heat} \underset{\text{major}}{CH_3CH_2Br} + \underset{\text{trace amounts}}{CH_3CH_2CH_2CH_3}$$

IV.



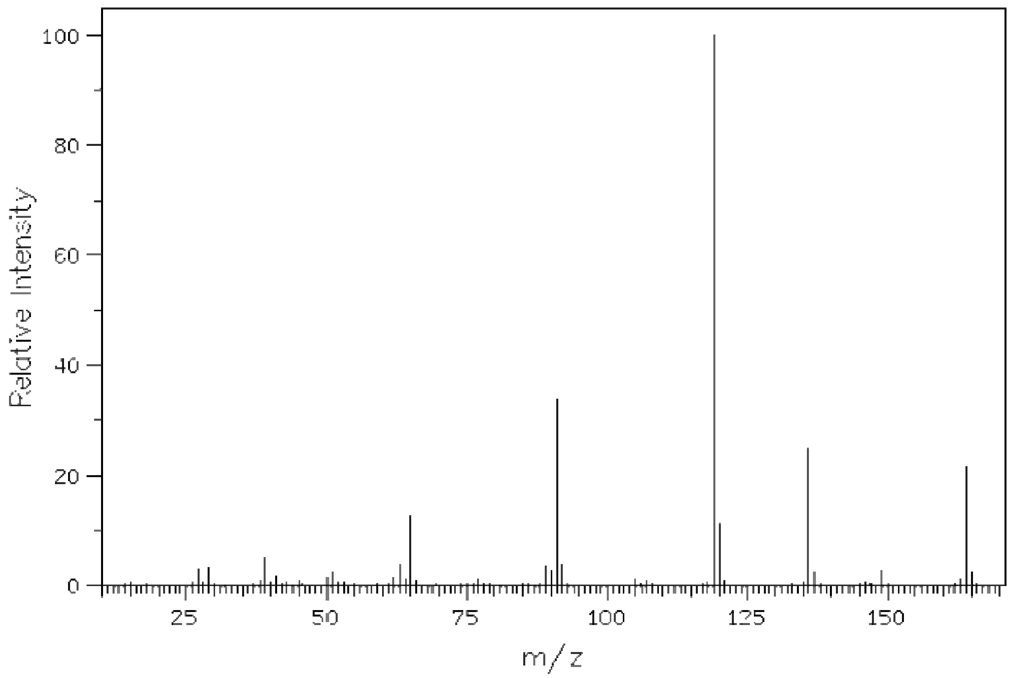
PART 8: SPECTROSCOPY

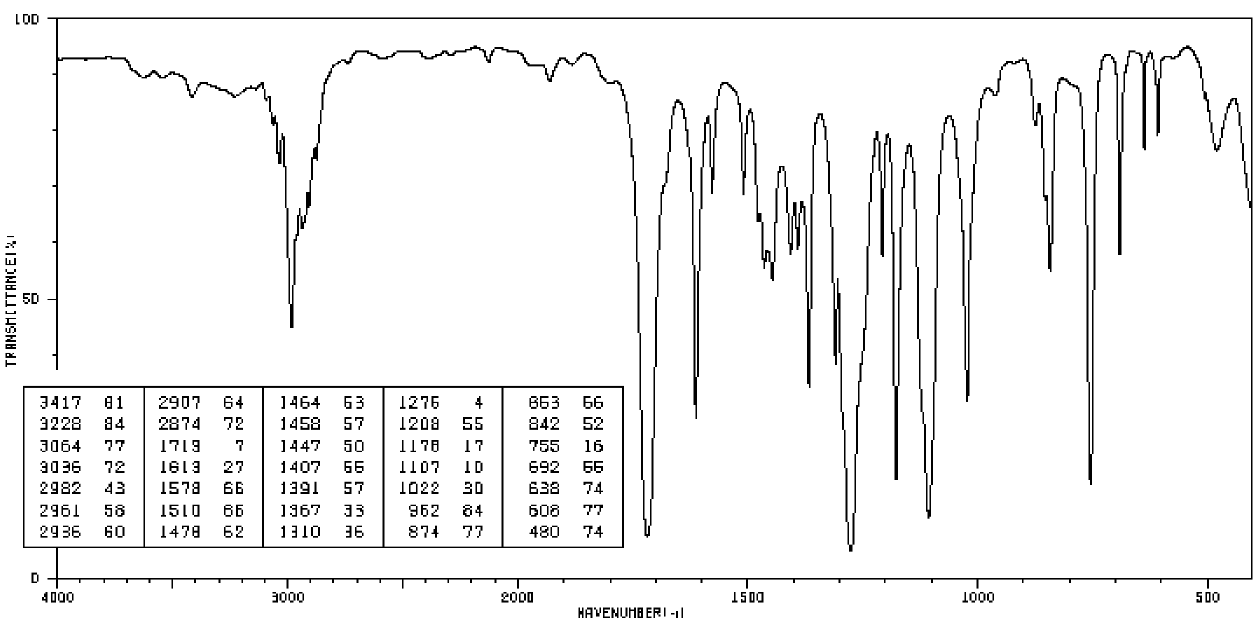
10% **WRITE YOUR ANSWERS IN THE BOOKLET PROVIDED**

Show your workings as PARTIAL marks will be given.

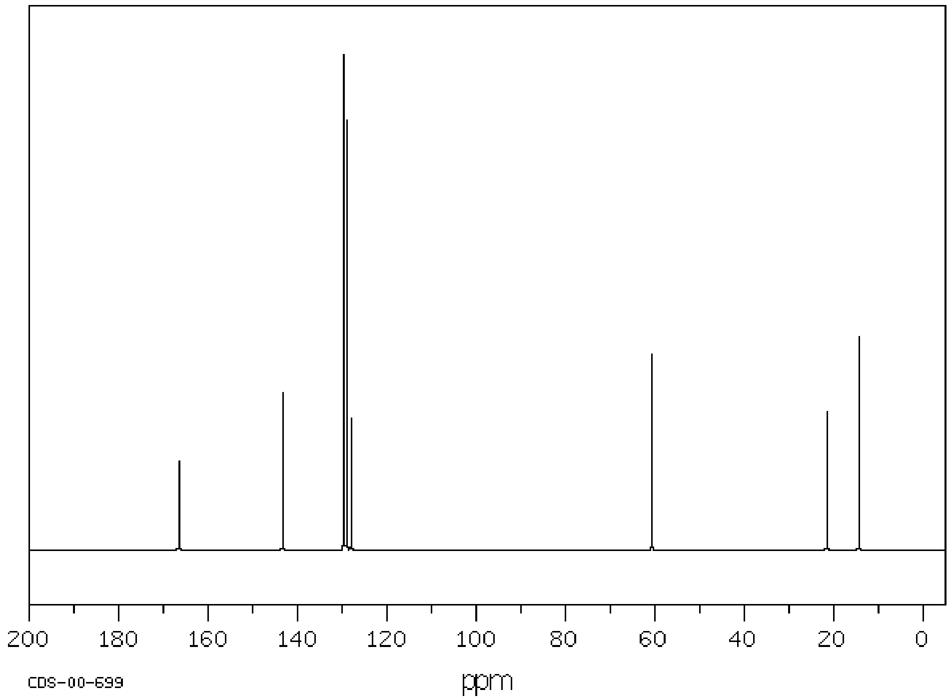
From the data provided below, identify the structure of the "unknown" molecule.

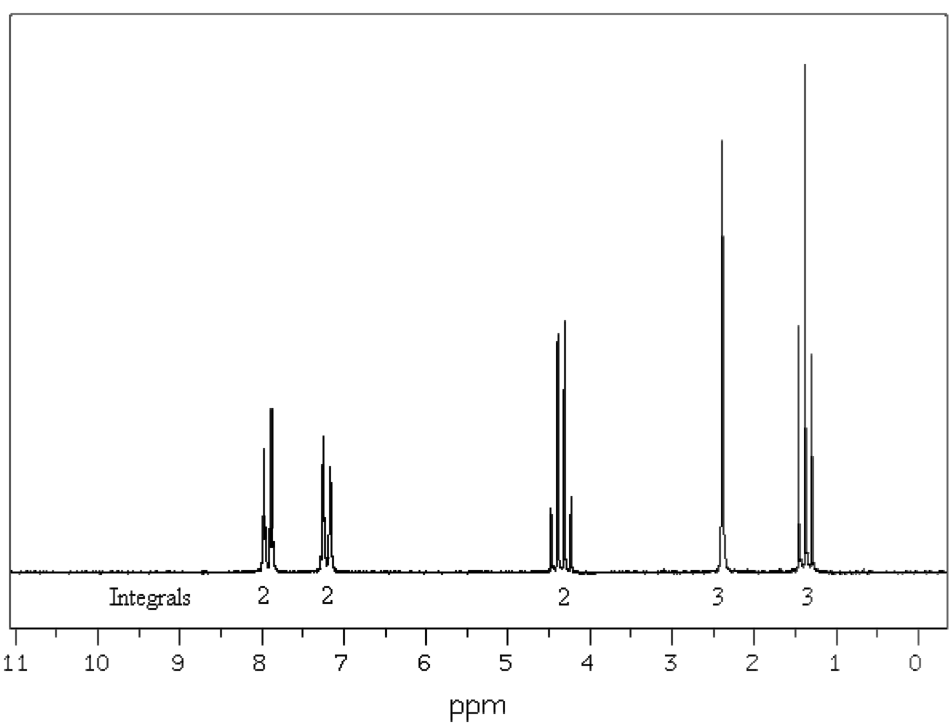
Elemental analysis : 73.15 % C and 7.37 % H (by weight).





3417	81	2907	64	1464	63	1276	4	853	66
3228	84	2874	72	1458	57	1208	55	842	52
3064	77	1719	7	1447	50	1178	17	755	16
3036	72	1613	27	1407	66	1107	10	692	66
2982	43	1578	66	1391	57	1022	30	638	74
2961	58	1510	66	1367	33	962	84	606	77
2936	60	1478	62	1310	36	874	77	480	74


200
180
160
140
120
100
80
60
40
20
0
CDS-00-699
ppm


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

PART 9: STRUCTURE DETERMINATION

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

Hydrocarbon **A**, C_6H_{14}, was reacted with Br_2 / uv light to give **B**, $C_6H_{13}Br$ as the major product. Subsequent reaction of **B** by heating with KOH / EtOH / heat gave a new hydrocarbon **C**, C_6H_{12} (IR absorption : 1650 cm^{-1}). It was found that **C** could be converted back to **A** using H_2 / Pd catalyst.

Reaction of **B** with H_2O / Na_2CO_3 gave **D**, $C_6H_{14}O$ (IR absorption : 3500 cm^{-1}, broad). When **D** was reacted with HBr compound **E** an isomer of **B** was obtained. Subsequent reaction of **E** by heating with KOH / EtOH / heat gave **F** an isomer of **C** (IR absorption : 1650 cm^{-1}).

Oxidation of **D** with a chromate reagent gave **G**, $C_6H_{12}O$ (IR absorption : 1715 cm^{-1}).

Compounds **A**, **B**, **C**, **D**, **E** and **G** all had 4 peaks in the ^{13}C nmr and **F** has only 2 peaks.

Identify the compounds **A-G**.

**** THE END ****