THE UNIVERSITY OF CALGARY

FACULTY OF SCIENCE

FINAL EXAMINATION

CHEMISTRY 351

December 16th, 2005

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 - 42, which are to be answered on your computer answer sheet. Indicate your answer by blackening out the appropriate space, A, B, C, D or E on the answer sheet. Use a pencil only and ***not ink***. In some cases it is required that you indicate ***multiple*** items for a complete and/or correct answer by blackening out more than one space. In some other cases more than five options are available and some of these also require more than one space to be blackened out. For an example, an option specified as AB requires that you blacken out ***both*** space A and space B. Part marks may be awarded in some of the questions. Incorrect answers must be erased ***cleanly***.

Molecular models are permitted during the exam; calculators are also permitted, ***but NOT programmable calculators***.

Absolutely no other electronic devices are allowed.

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20% PART 1 RELATIVE PROPERTIES

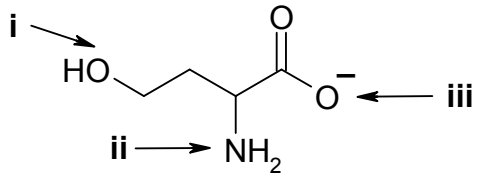
ANSWER ANY TEN (10) OF QUESTIONS 1 TO 12.

Arrange the items in questions 1-12 in DECREASING ORDER (i.e. greatest, most etc. first) with respect to the indicated property.

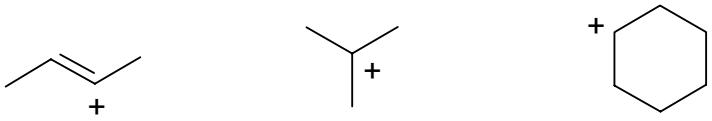
Use the following code to indicate your answers

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 basicity of the **atoms** indicated in the following structure :

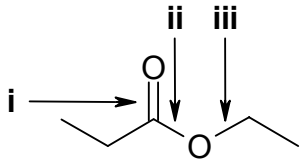


2. The relative stability of the following carbocations :

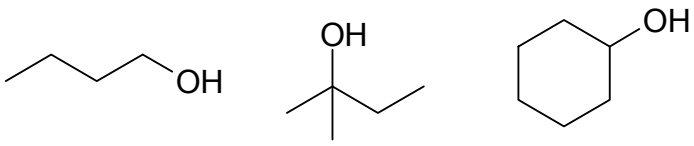


i **ii** **iii**

3. The stretching frequency in the infrared spectrum of the CO bonds indicated below:



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



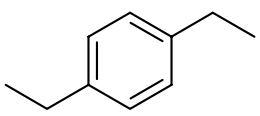
i **ii** **iii**

Cont'd -->

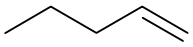
Use the following code to indicate your answers

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

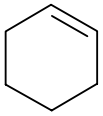
5. The number of peaks expected in the normal proton decoupled ^{13}C NMR spectrum for each of the following:



i

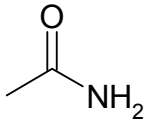


ii

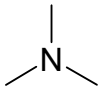


iii

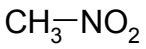
6. The relative basicity of the **nitrogen atom** in each of the following :



i

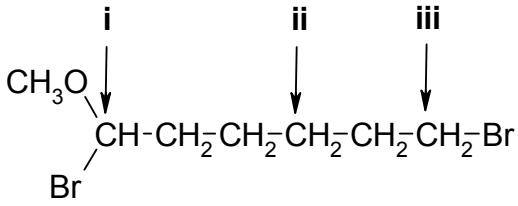


ii

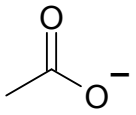


iii

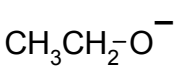
7. The ^{1}H-NMR chemical shifts for the groups indicated in the following structure :



8. The relative rates of reaction of each of the following towards 2-bromobutane :



i



ii

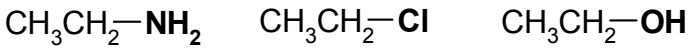
iii

Cont'd -->

Use the following code to indicate your answers

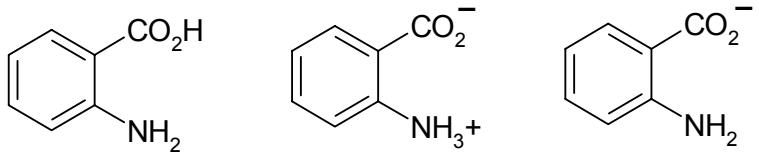
A.	**i > ii > iii**	**D**.	**ii > iii > i**
B.	**i > iii > ii**	**E**.	**iii > i > ii**
C.	**ii > i > iii**	**AB**.	**iii > ii > i**

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



i **ii** **iii**

10. The relative amounts of the following ions produced when an aqueous solution of anthranilic acid (also called *ortho*-aminobenzoic acid) is reacted with 0.25 mole equivalents of NaOH:

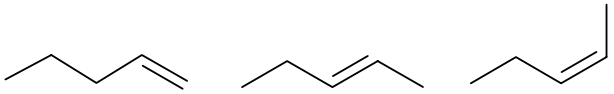


i **ii** **iii**

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-bromopentane
ii chlorocyclopentane
iii 2-bromo-2-methylbutane

12. The relative heats of formation of the following alkanes (least exothermic to most exothermic):



i **ii** **iii**

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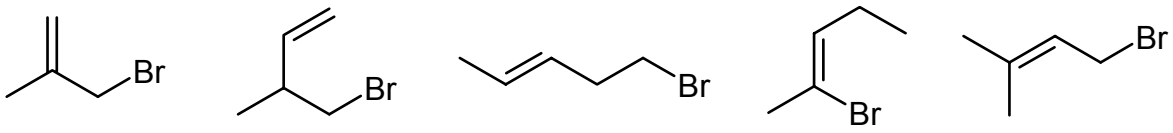
8% PART 2: LABORATORY

ANSWER ALL FIVE (5) OF THE QUESTIONS 13-17.

Questions 13-17 are based on the laboratory component of the course.

Questions 13-14 refer to the following molecules:



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

13. Based on the "Reactivity in Substitution Reactions" experiment, which molecule would be expected to react the fastest using $AgNO_3$ in water-ethanol ?

14. Based on the "Reactivity in Substitution Reactions" experiment, which molecule would react the slowest using NaI in acetone ?

In questions 15-17 select ALL the correct answers. In some questions, MORE THAN ONE ANSWER MAY BE CORRECT.

15. Which of the following molecules has / have an IHD of 2 ?

    A Ethyl ethanoate
    B Cyclohexanol
    C Propionitrile
    D Cyclohexanone
    E 2-Methoxybutanal

Cont'd -->

16. Which of the following statements about the caffeine experiment is / are true ?

A Caffeine is more soluble in water than in dichloromethane

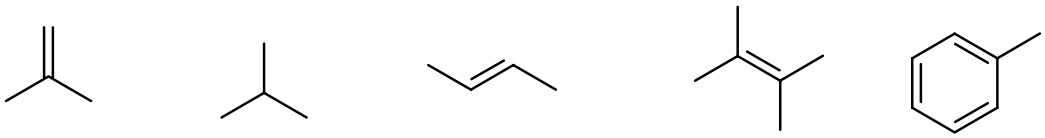
B Caffeine can sublime

C Caffeine is very soluble in petroleum ether

D In a separating funnel that contains water and dichloromethane, the lower layer is the organic liquid

E A “cold finger” is used to remove the organic solvent

17. In the experiment about the reaction of bromine with hydrocarbons which of the following starting materials would give a major product that had only one singlet peak in its proton NMR spectrum ?

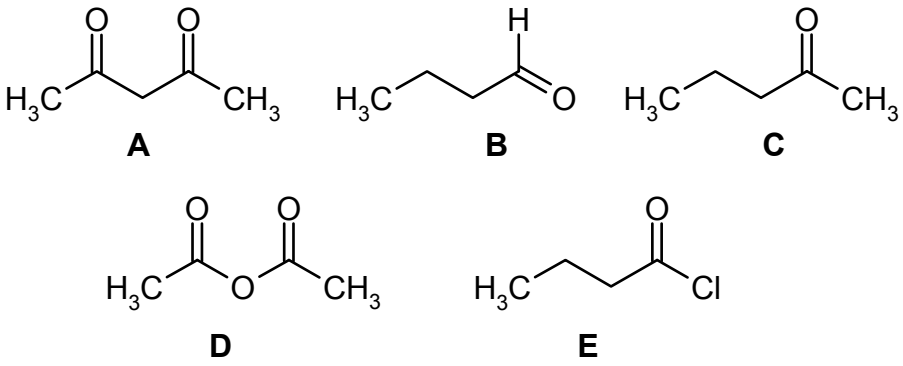


A **B** **C** **D** **E**

10% PART 3: MOLECULAR PROPERTIES

ANSWER ALL TEN (10) of the questions 18-27.

Use the following information and structures A-E to answer questions 18 - 20

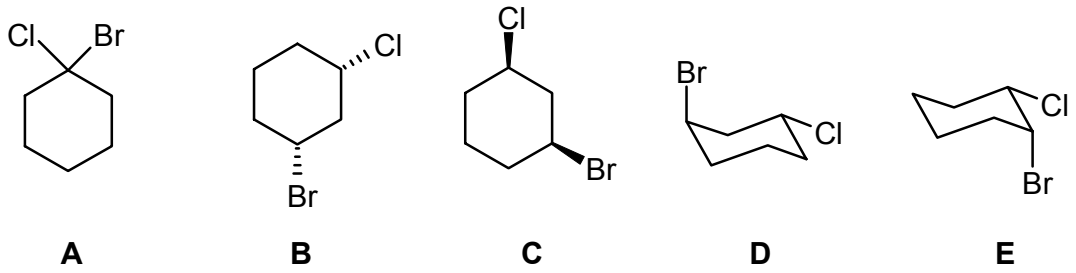


18. Which structure has the most acidic hydrogen atom ?

19. Which structure has the hydrogen that would have the furthest downfield chemical shift in its proton NMR spectrum ?

20. Which structure is a constitutional isomer of propenyl ethanoate ?

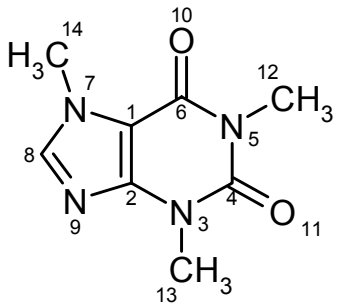
Use the following list of structures to answer questions 21 and 22.



21. Select any two molecules that would have the same melting points

22. Select an isomer that has no chiral centres

For each of the questions about CAFFEINE (right), select the answer from those provided.



23. What is the index of hydrogen deficiency (IHD) of **CAFFEINE** ?

A. 2 **B**. 3 **C**. 4 **D**. 5 **E**. 6

24. How many types of hydrogen are there in **CAFFEINE** ?

A. 1 **B**. 2 **C**. 3 **D**. 4 **E**. 5

25. In **CAFFEINE**, what are the hydridisations of **C1, N3, and O10** respectively:

A. sp^3, sp^2, sp^2 **B**. sp^2, sp^3, sp^3 **C**. sp^2, sp^2, sp^3
D. sp^3, sp^3, sp^2 **E**. sp^2, sp^3, sp^2 **AB.** sp^2, sp^2, sp^2

26. In **CAFFEINE**, what are the oxidation states of **N3** and **C6** respectively ?

A. -2, +3 **B**. -2, -1 **C**. -3, -1 **D**. –3, +3 **E**. –3, -3

27. How many carbon signals would be expected in the ^{13}C-NMR spectrum of **CAFFEINE** ?

A. 4 **B**. 5 **C**. 6 **D**. 7 **E**. 8

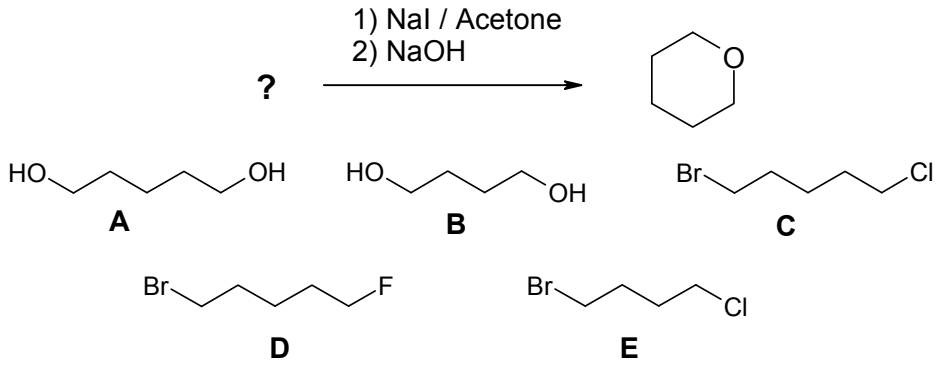
Cont'd -->

12% PART 4: REACTIONS

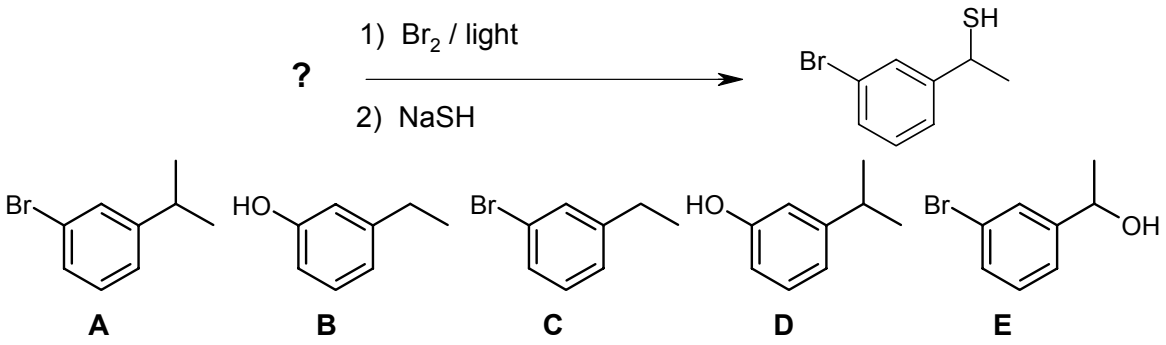
ANSWER ANY EIGHT (8) OF QUESTIONS 28-36.

For each of questions 28-36 select the MISSING component (the starting material, the product or the reagents) required in order to BEST complete each of the reaction schemes.

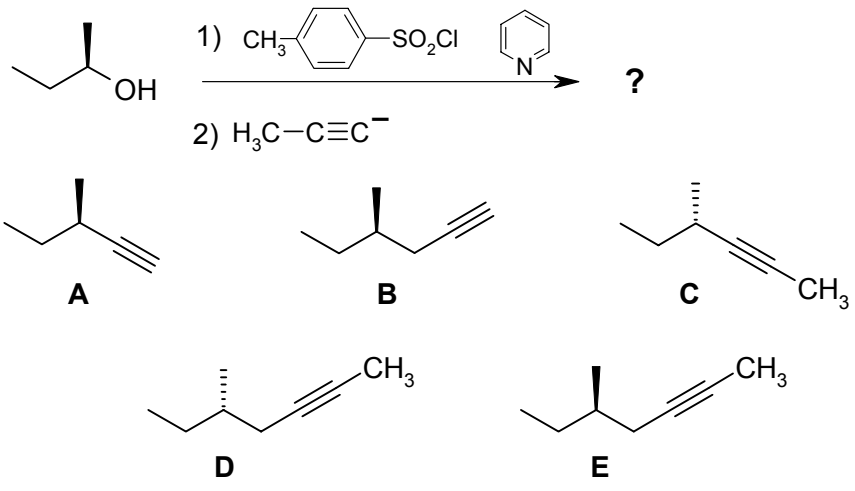
28.



29.



30.



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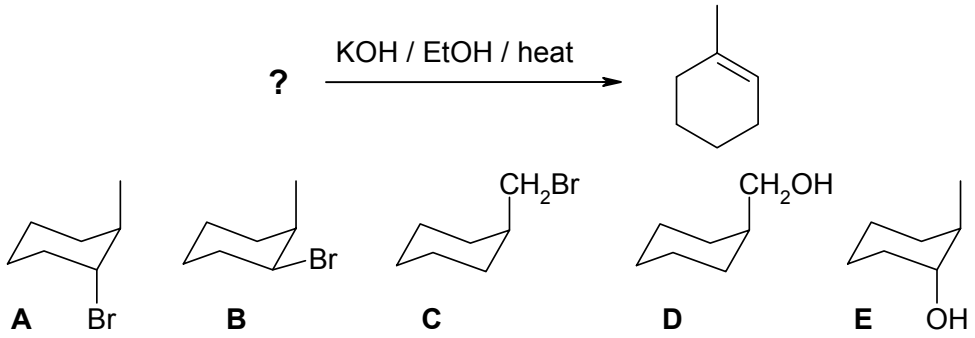
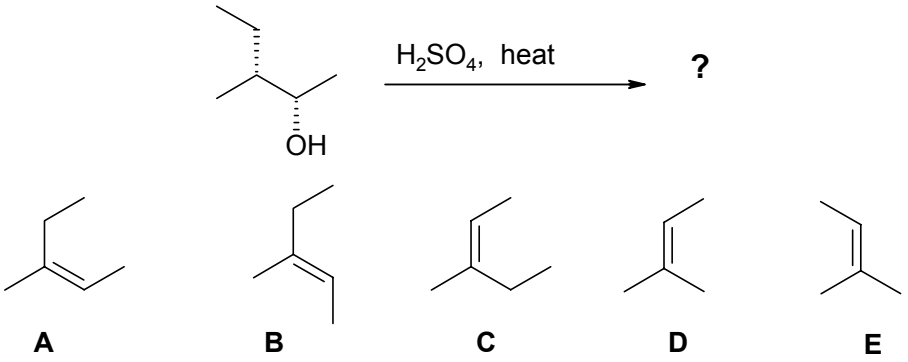
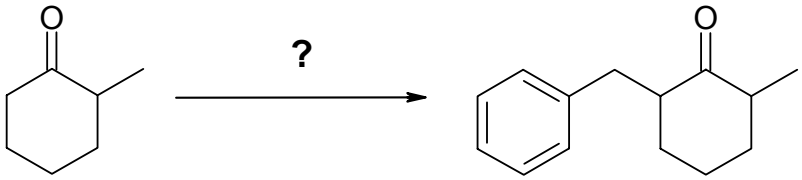
31.



32.



33.



A 1. Na, ether 2. Benzyl alcohol

B 1. Br_2, uv light 2. Benzyl bromide

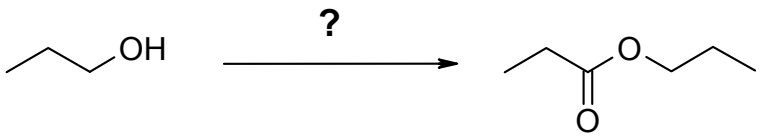
C 1. Br_2, uv light 2. Benzyl alcohol

D 1. $NaNH_2$ 2. Phenyl Bromide

E 1. $NaNH_2$ 2. Benzyl Bromide

Cont'd -->

34.



A. Acetic anhydride, pyridine

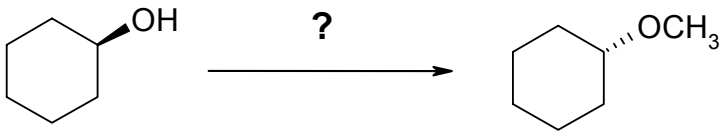
B. 1. TsCl, pyridine 2. $CH_3CH_2CO_2^-$

C. Conc. H_2SO_4, heat

D. 1. Br_2, heat 2. $CH_3CH_2CO_2^-$

E. KOH, $CH_3CH_2CH_2OH$, heat

35.



A. Acetic anhydride, pyridine

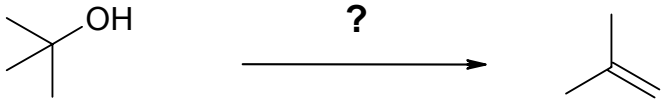
B. CH_3OCH_3, heat

C. $NaOCH_3$, heat

D. 1. HBr 2. CH_3OCH_3, heat

E. 1. TsCl, pyridine 2. $NaOCH_3$

36.



A. KOH / EtOH / heat

B. conc. H_2SO_4 , heat

C. 1. NaBr, DMF, heat 2. conc. H_2SO_4 , heat

D. PBr_3, NEt_3 2. conc. H_2SO_4 , heat

E. 1. Br_2 / uv light 2. conc. H_2SO_4 , heat

Cont'd -->

9% 12% PART 5: SPECTROSCOPY

ANSWER ALL SIX (6) OF QUESTIONS 37 - 42.

For each of questions 37-42 select the compound from the list provided that corresponds BEST with the spectroscopic data provided. The following common abbreviations have been used s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, m = multiplet

37. **^{1}H-NMR**: δ/ppm 0.9 (t, 3H), 1.5 (sextet, 2H), 2.0 (t, 2H), 6.7 (s, 1H), 7.2 (s, 1H)
^{13}C-NMR: δ/ppm 13.7, 19.0, 37.9, 176.4
IR: 3356, 3184, 1660 cm^{-1}

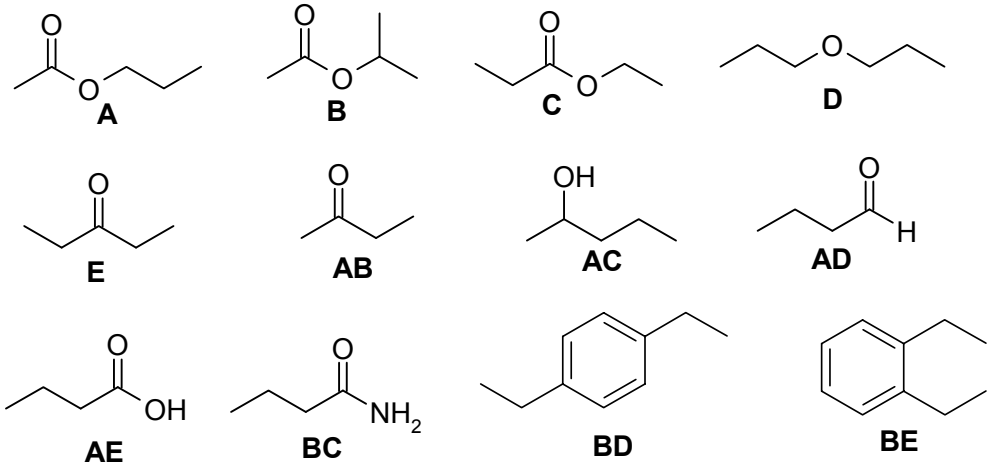
38. **^{1}H-NMR**: δ/ppm 1.0 (t, 3H), 1.7 (sextet, 2H), 2.3 (t, 2H), 11.5 (s, 1H, D_2O exchange)
^{13}C-NMR: δ/ppm 13.7, 18.4, 36.2, 180.7
IR: 2700-3300, 1712 cm^{-1}

39. **^{1}H-NMR**: δ/ppm 1.0 (t, 3H), 2.4 (q, 2H)
^{13}C-NMR: δ/ppm 7.9, 35.5, 212
IR: 1720 cm^{-1}

40. **^{1}H-NMR**: δ/ppm 0.9 (t, 3H), 1.2 (d, 3H), 1.32-1.48 (m, 4H), 2.6 (s, 1H, D_2O exchange), 3.8 (sextet, 1H)
^{13}C-NMR: δ/ppm 14.1, 19.0, 23.4, 41.6, 67.7
IR: 3100-3500 cm^{-1}

41. **^{1}H-NMR**: δ/ppm 1.22 (t, 3H), 2.64 (q, 2H) 7.14 (m, 2H)
^{13}C-NMR: δ/ppm 15.4, 25,5, 141.6, 126, 128.3
IR: 1489, 1461 cm^{-1}

42. **^{1}H NMR** : δ/ppm 1.0 (t, 3 H), 1.6 (sextet, 2 H), 2.0 (s, 3 H), 4.1 (t, 2 H).
^{13}C-NMR: δ/ppm 10.4, 20.9, 22.1, 66.1, 171
IR = 1745 cm^{-1}



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6% PART 6: SYNTHESIS

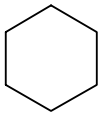
DESIGN EFFICIENT SYNTHESES OF ANY TWO (2) of the following target molecules using any of the starting materials shown below.

WRITE YOUR ANSWERS IN THE BOOKLET PROVIDED.

DO NOT SHOW MECHANISMS.

TARGETS

Allowed Starting Materials:



any **hydrocarbon** with 3 or less C atoms

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

Cont'd -->

10% **PART 7: MECHANISMS**

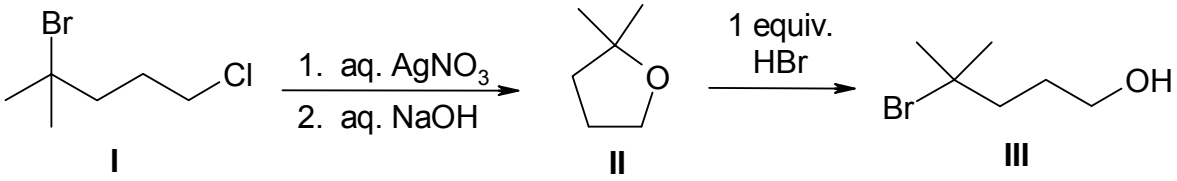
WRITE YOUR ANSWERS IN THE BOOKLET PROVIDED

ANSWER EITHER QUESTION I or II.

Draw curly arrow mechanisms to answer / explain the following reactions / observations. No other reagents are required.

EITHER

I.



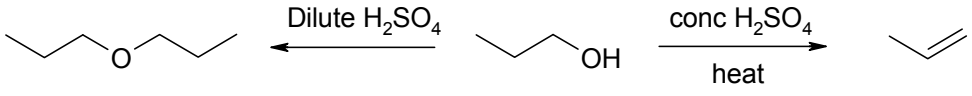
I **II** **III**

i Show the mechanism for the transformation of **I** to **II**.

ii Show the mechanism for the transformation of **II** to **III**.

OR

II.



Reaction A **Reaction B**

i For **reaction A**, show the mechanism for the formation of dipropyl ether.

ii For **reaction B**, show the mechanism for the formation of propene.

iii One of the alcohols shown below readily undergoes elimination and nucleophilic substitution reactions, while the other does not. From a mechanistic view point, (showing mechanisms etc) rationalise this difference.

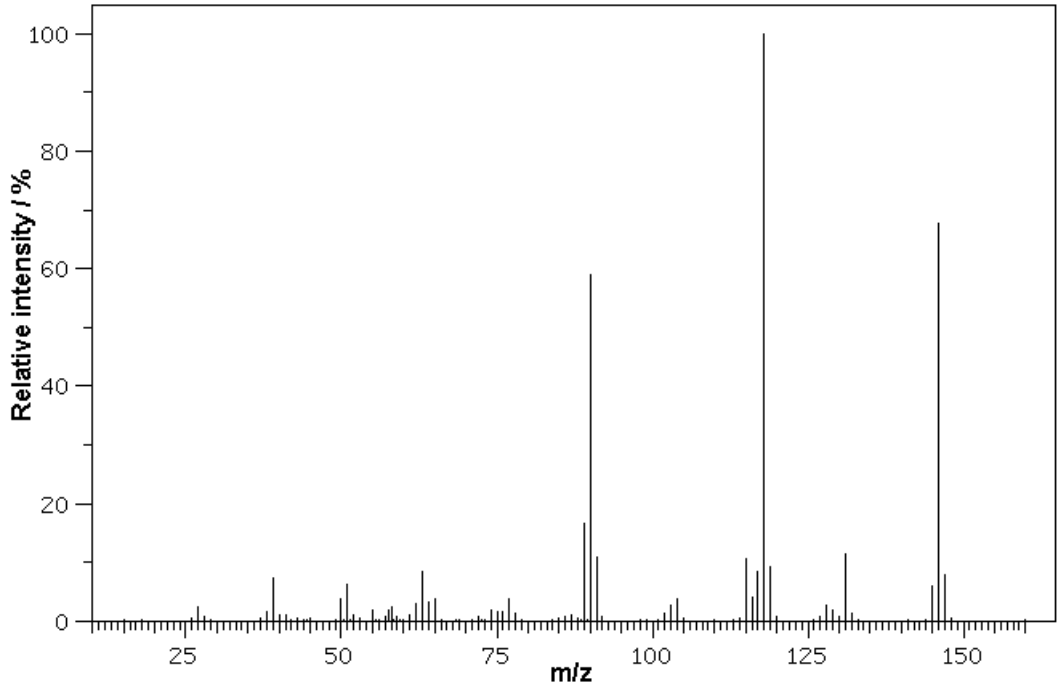
Cont'd -->

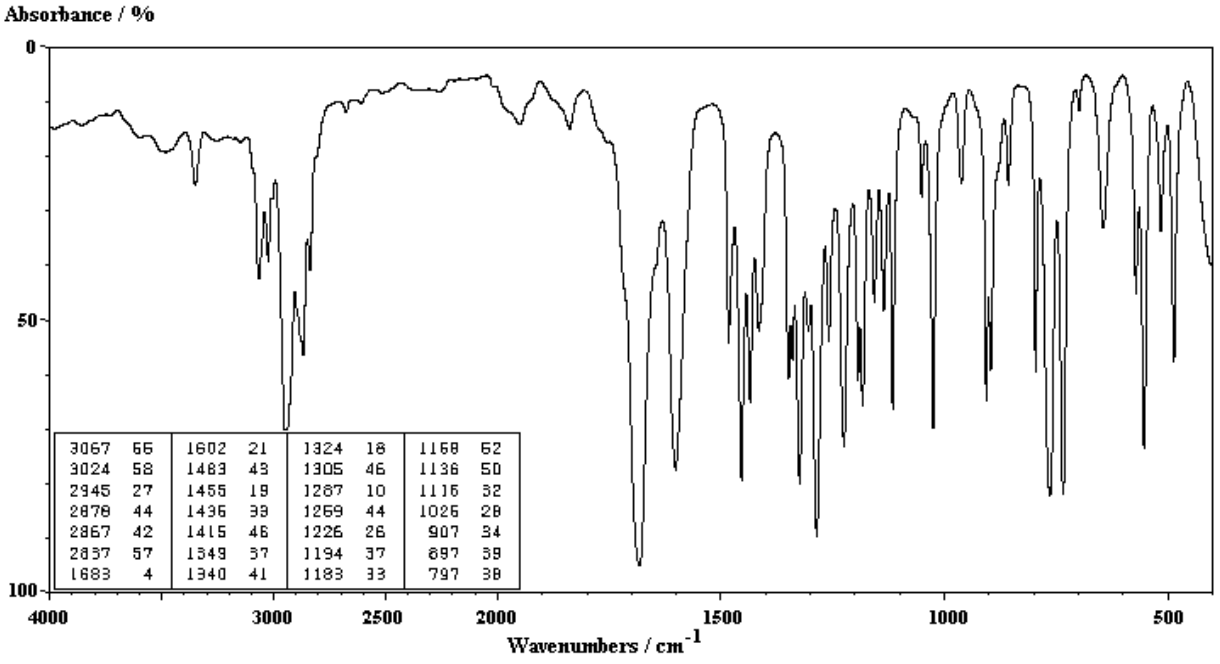
10% PART 8: SPECTROSCOPY

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 and N only : 82.19% C, 6.85% H





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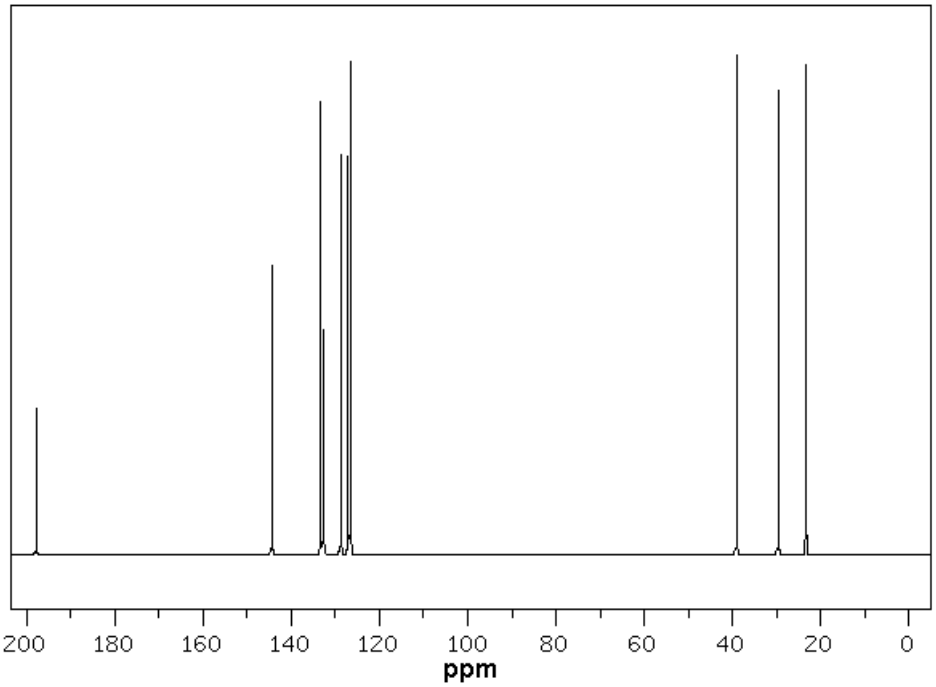

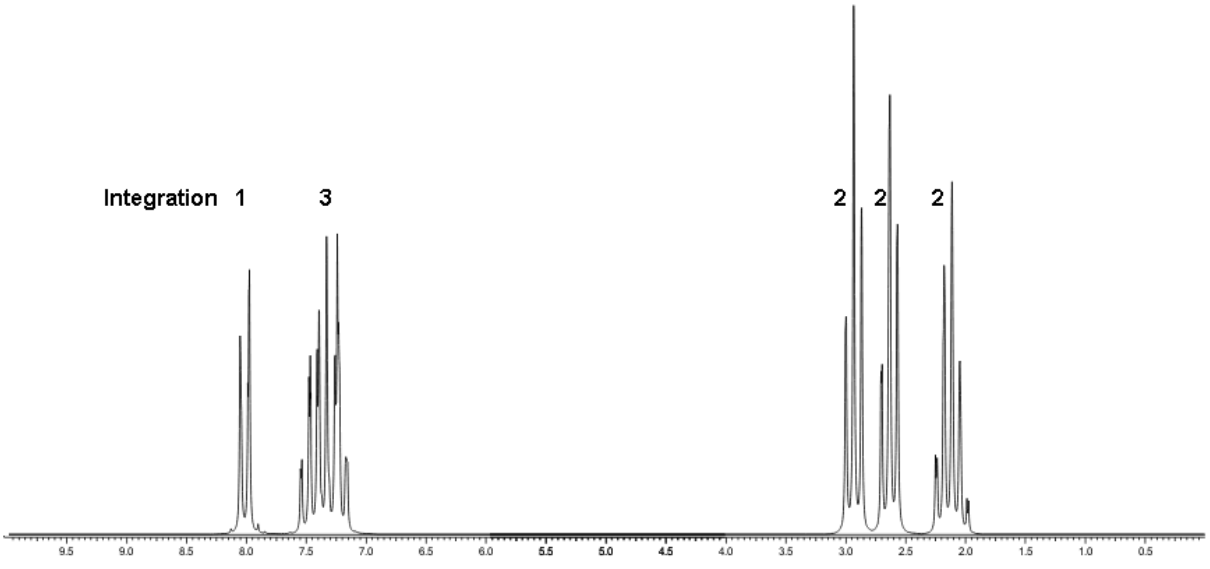

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12% PART 9: STRUCTURE DETERMINATION

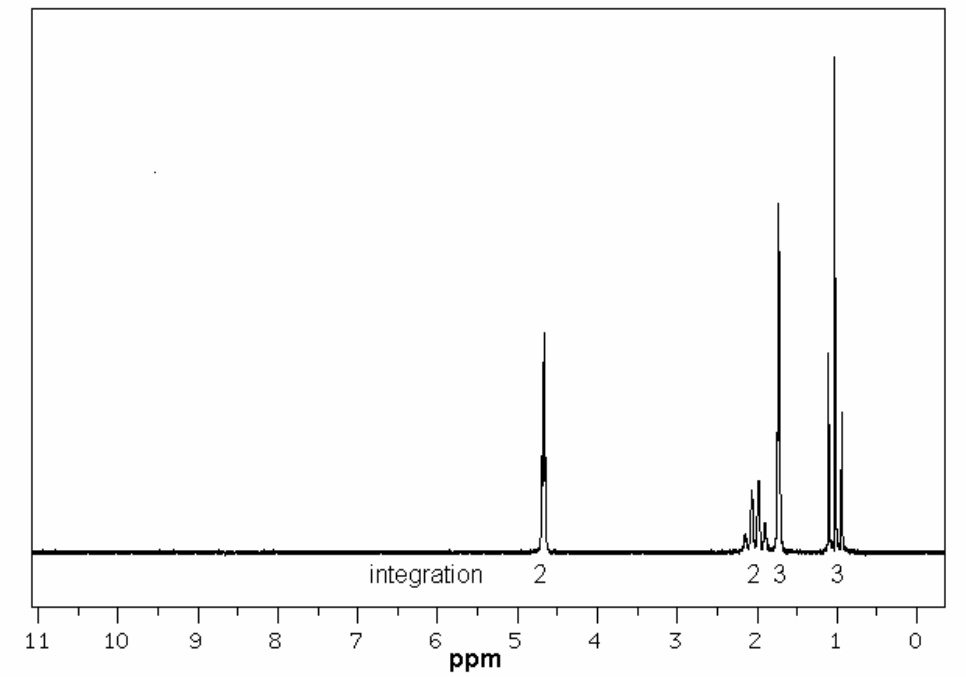
WRITE YOUR ANSWERS IN THE BOOKLET PROVIDED

An achiral hydrocarbon **A**, C_5H_{12}, was reacted with Br_2 / UV light to give a single product **B**, $C_5H_{11}Br$. **B** did not react with potassium *tert*-butoxide in *tert*-butanol. **B** was reacted with aqueous NaOH to give **C** (the IR of **C** showed a broad peak at 3500 cm^{-1}).

When reacted with HBr, **C** gave a major product **D**. When reacted with PBr_3 / triethylamine, **C** gave **B** as the major product. **D** and **B** have four and three types of carbon, respectively.

D was reacted with potassium *tert*-butoxide in *tert*-butanol to give **E** as the major product. **C** can be heated in concentrated H_2SO_4 to give a major product **F**.

The NMR spectrum of **E** is shown below.



- Identify **A-F** (only structures are needed).

**** THE END ****

IRH/AC : F2005