

THE UNIVERSITY OF CALGARY
FACULTY OF SCIENCE
FINAL EXAMINATION
CHEMISTRY 351

December 20th, 2004

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 - 41, 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**.

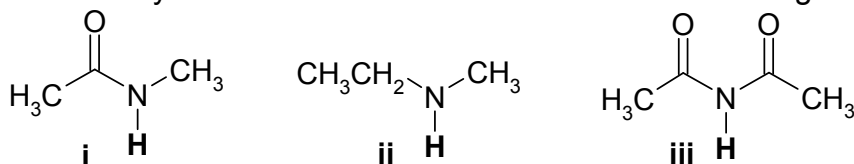
20% PART 1 RELATIVE PROPERTIES**ANSWER ANY TEN (10) OF QUESTIONS 1 TO 12.**

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

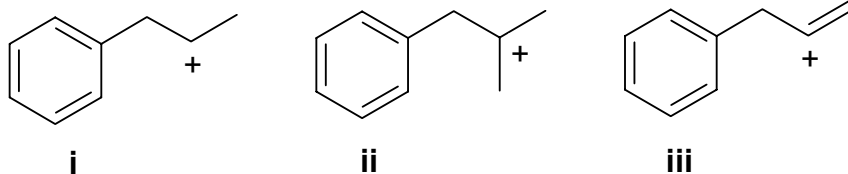
Use the following code to indicate your answers.

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

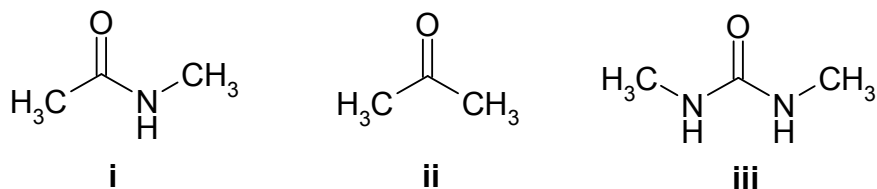
1. The relative acidity of the bold H atoms indicated in the following structures :



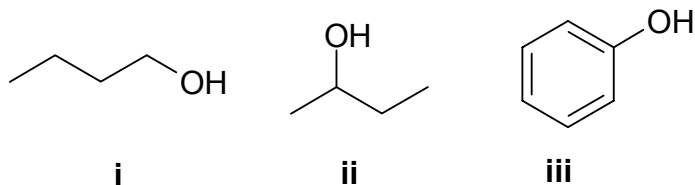
2. The relative stability of the following carbocations :



3. The carbonyl stretching frequency in the infrared spectrum of each of the following structures:



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



Use the following code to indicate your answers.

A. i > ii > iii

B. i > iii > ii

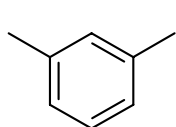
C. ii > i > iii

D. ii > iii > i

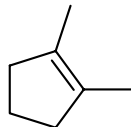
E. iii > i > ii

AB. iii > ii > i

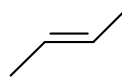
5. The number of peaks seen in the normal broadband proton decoupled ^{13}C NMR spectrum for each of the following:



i

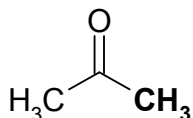


ii

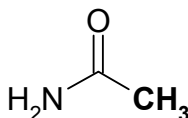


iii

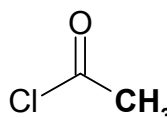
6. The ^{13}C NMR chemical shifts for the groups shown in **bold** in each of the following structures :



i

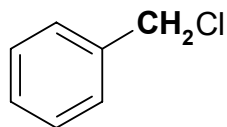


ii

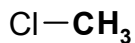


iii

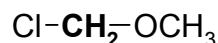
7. The ^1H -NMR chemical shifts for the groups shown in **bold** in each of the following structures :



i

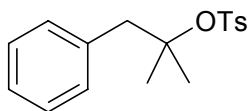


ii

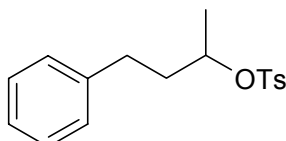


iii

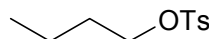
8. The relative rates of reaction of each of the following with NaCN :



i



ii

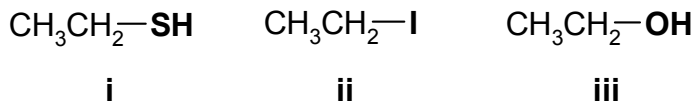


iii

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



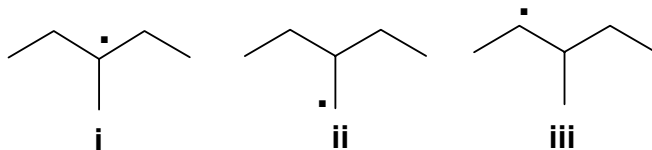
10. The relative amount of the conjugate base of 2-propanone formed (an enolate) by the reaction of 1 mole equivalent of each of the following:

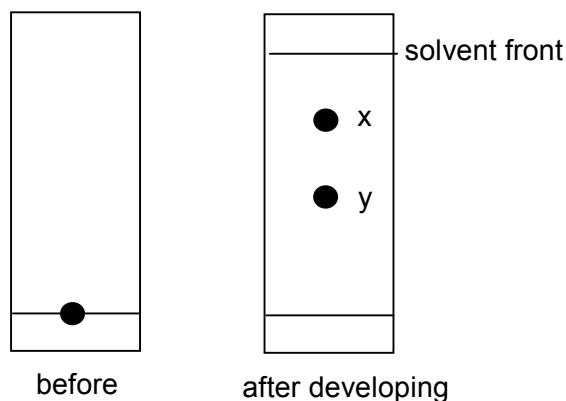


11. The number of possible alkene isomers that could be produced by the reaction of each of the following by heating with ethanolic KOH :

- i** 1-bromopentane
- ii** 3-bromopentane
- iii** 3-chloro-3-methylpentane

12. The relative stability of the following radicals:



11% PART 2: LABORATORY**ANSWER ALL FIVE (5) OF THE QUESTIONS 13-17.****Questions 13-17 are based on the laboratory component of the course.**

13. What is the R_f value for the sample spot "y" shown on the normal chromatographic plate after development (see diagram above) ?

- A** 2 **B** 1 **C** 0.75 **D** 0.5 **E** 0.25

14. Which of the following 3 statements about the chromatographic plate above are correct ?

- i** the original sample is probably impure.
- ii** sample "x" is more polar than "y"
- iii** sample "y" eluted more rapidly than sample "x"

- A** only **i** is true **B** only **ii** is true **C** only **iii** is true
D only **i** and **ii** are true **E** only **i** and **iii** are true **AB** **i**, **ii** and **iii** are true

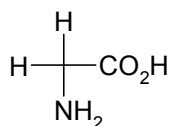
In questions 15-17 select the ALL statements that are true. In some questions, MORE THAN ONE STATEMENT MAY BE TRUE.

15. Based on the molecular models exercise, which of the following statements are true ?

- A** benzene, C_6H_6 has an index of hydrogen deficiency = 3
- B** 1,2-dichlorobenzene has 3 types of carbon.
- C** adamantane (see below) has 2 types of hydrogen.



- D** The amino acid glycine (see below) is chiral



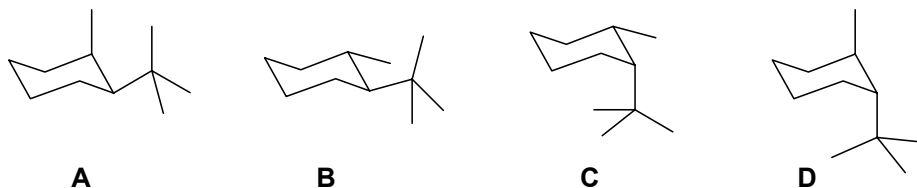
- E** 2,3-pentadiene has a non-superimposable mirror image.

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

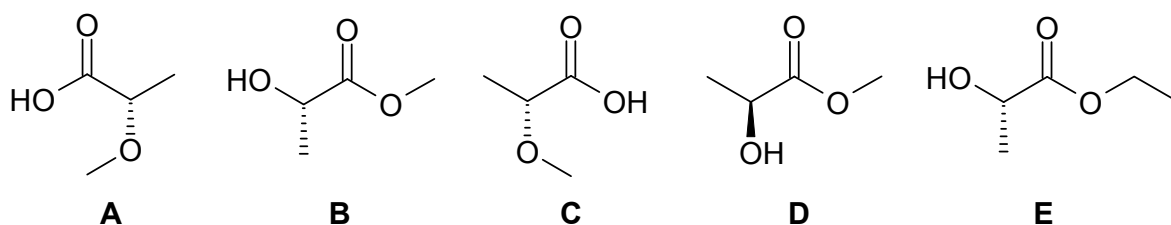
- A** acetone is an example of a nonpolar, aprotic solvent.
- B** sodium chloride is insoluble in acetone.
- C** sodium iodide / acetone indicates S_N2 reactivity.
- D** bromides are more reactive than chlorides.
- E** t-butyl bromide reacted more rapidly than n-butyl bromide.

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

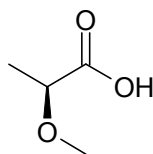
- A** bromine reacts with alkanes to give 1,2-dibromides.
- B** for alkanes the controlling factor is radical stability.
- C** cyclohexane reacts more rapidly than methylbenzene.
- D** alkanes react with halogens via radical substitution.
- E** t-butylbenzene reacted slowly because it's sterically hindered.

10% PART 3: MOLECULAR PROPERTIES**ANSWER ALL TEN (10) of the questions 18-27****Use the following information and structures A-D to answer questions 18 - 20****The heats of formation, ΔH_f for the four isomers shown below are, in random order, -13.5 , -11.5 , -9.7 , and -9.5 kcal/mol.**18. Which isomer has a ΔH_f of -13.5 kcal/mol?19. Which isomer has will have the most exothermic heat of combustion, ΔH_c ?

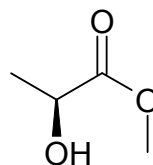
20. Which isomer has the largest amount of Van der Waal's strain?

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

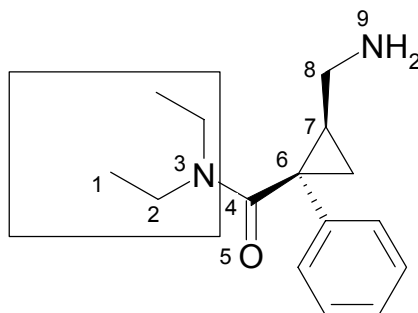
21. Select a constitutional isomer of :



22. Select a conformational isomer of:



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



23. How many optical isomers of **MILNACIPRAN** are there including the one shown?

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

24. How many types of carbon are there in **MILNACIPRAN** ?

- A. 8 B. 10 C. 11 D. 13 E. 15

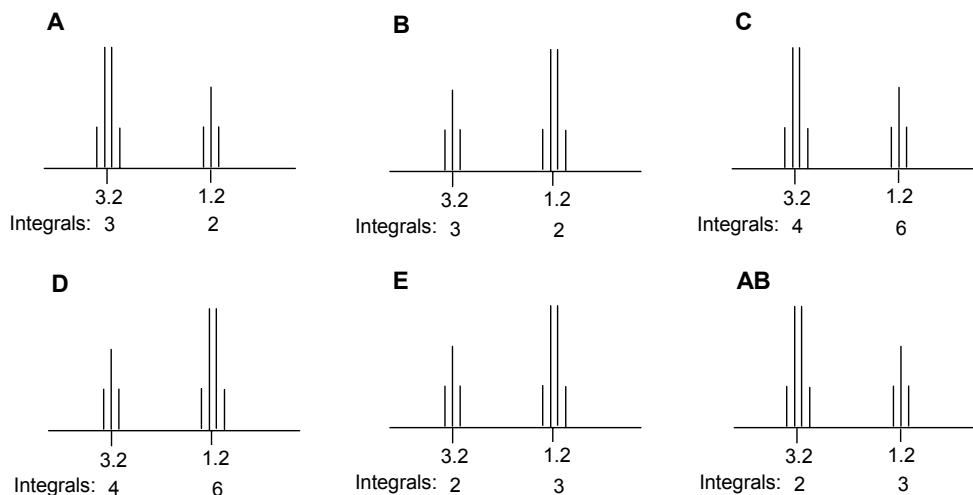
25. In **MILNACIPRAN**, what are the hybridisations of **O5**, **C7**, and **N9** respectively:

- A. sp^3 , sp^3 , sp^3 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 **MILNACIPRAN**, what are the oxidation states of **C4** and **C7** respectively ?

- A. +2, 0 B. +3, -1 C. +2, -1 D. -3, +1 E. -2, +1

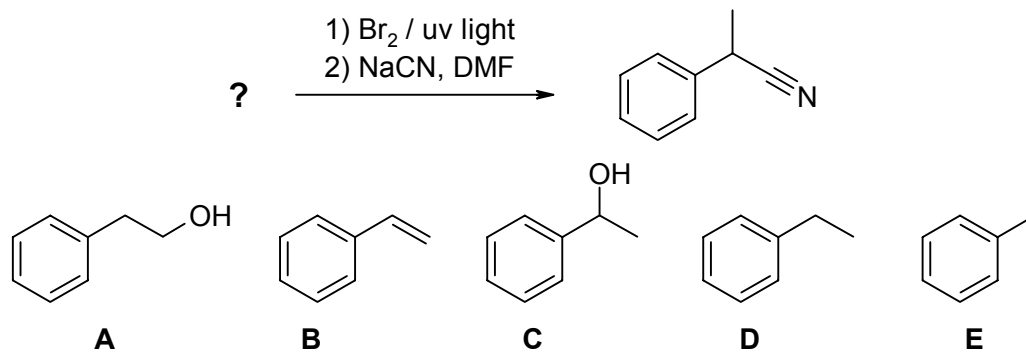
27. In a $^1\text{H-NMR}$ spectrum of **MILNACIPRAN**, which of the following figures best match the signals for the group in the rectangular box ?



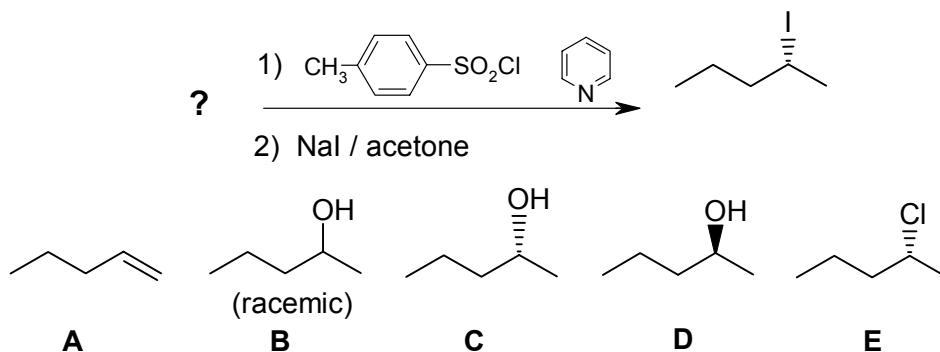
12% **PART 4: REACTIONS****ANSWER ANY EIGHT (8) OF QUESTIONS 28-36.**

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.

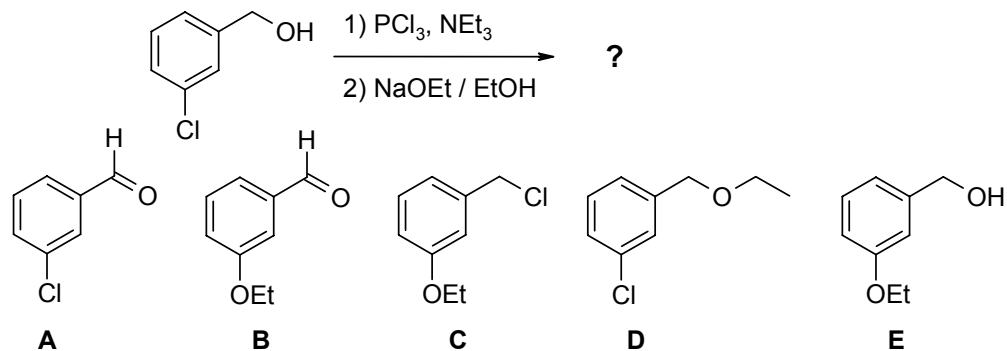
28.



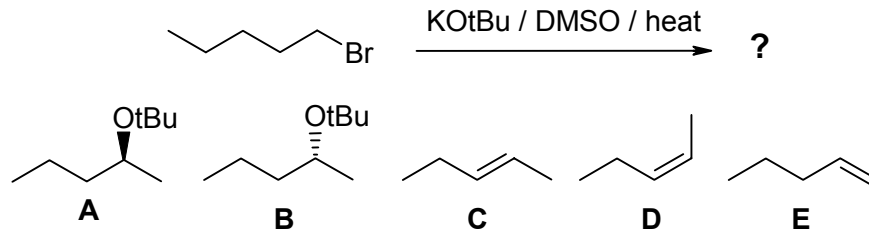
29.



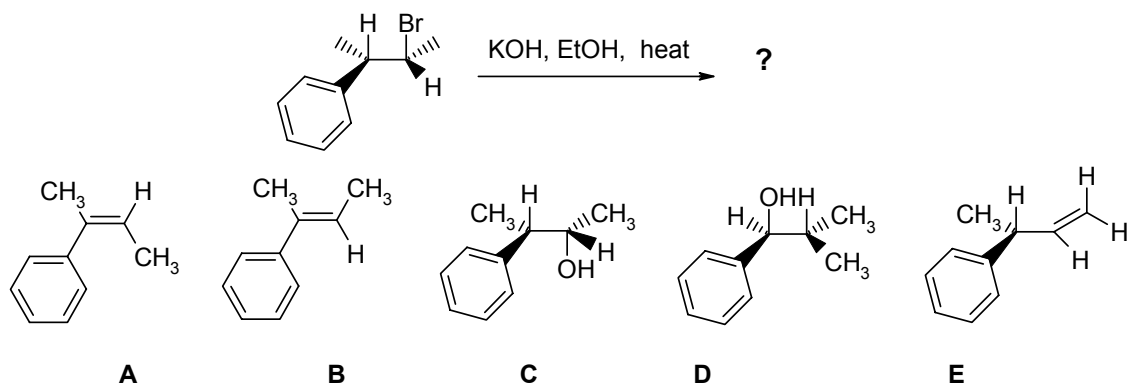
30.



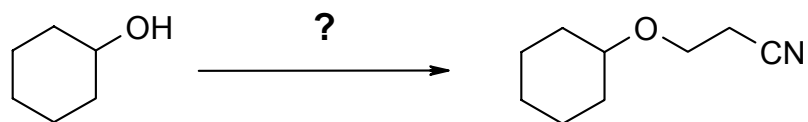
31.



32.

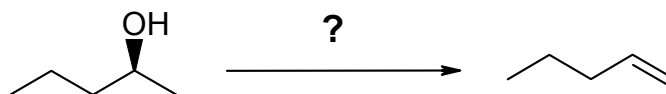


33.



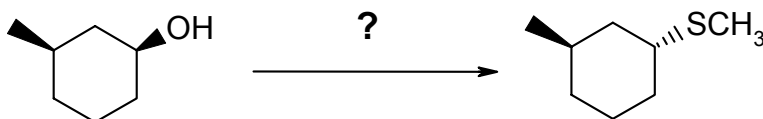
- A** 1. Na, ether 2. ClCH₂CH₂I 3. NaCN, DMF
B 1. HOCH₂CH₂Br 2. NaCN, DMF
C 1. Br₂, uv light 2. HOCH₂CH₂CN
D 1. TsCl, pyridine 2. BrCH₂CH₂CN
E 1. PBr₃, Et₃N 2. KOtBu, tBuOH 3. ClCH₂CH₂CN

34.



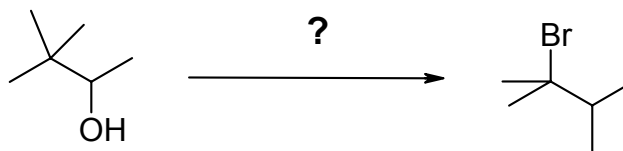
- A. 1. HBr, heat
- B. 1. TsCl, pyridine 2. KOtBu, HOTBu
- C. Conc. H₂SO₄, heat
- D. 1. HBr, heat 2. NaOCH₂CH₃, CH₃CH₂OH
- E. 1. KOH, CH₃CH₂OH, heat

35.



- A. 1. HBr, heat 2. NaSCH₃
- B. 1. TsCl, pyridine 2. NaSCH₃
- C. CH₃SH, HCl
- D. 1. Br₂ / uv light 2. NaSCH₃
- E. Pyridine, CH₃SH

36.

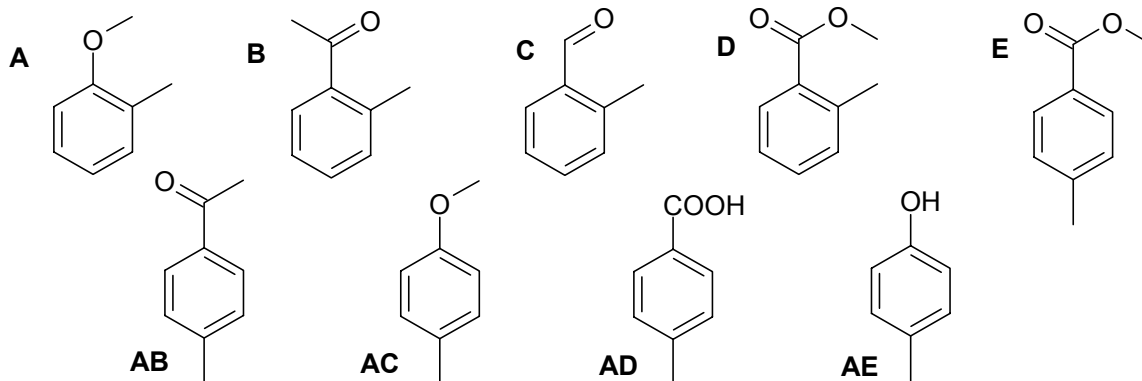


- A. 1. PBr₃, NEt₃ 2. NaBr, DMF
- B. HBr, heat
- C. NaBr, DMF, heat
- D. PBr₃, NEt₃
- E. Br₂ / uv light

10% PART 5: SPECTROSCOPY**ANSWER ALL FIVE (5) OF QUESTIONS 37 - 41.**

For each of questions 37-41 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, m = multiplet

37. $^1\text{H-NMR}$: δ/ppm 2.2 (s, 3H), 3.8 (s, 3H), 6.8 (m, 1H), 6.9 (m, 1H), 7.10 (m, 1H), 7.13 (m, 1H)
 $^{13}\text{C-NMR}$: δ/ppm 16.2, 55.1, 110.0, 120.4, 126.7, 126.9, 130.7, 157.9
 IR: 1246, 751 cm^{-1}
38. $^1\text{H-NMR}$: δ/ppm 2.4 (s, 3H), 2.5 (s, 3H), 7.2 (d, 2H), 7.8 (d, 2H)
 $^{13}\text{C-NMR}$: δ/ppm 21.5, 26.4, 128.4, 129.2, 134.8, 143.7, 197.5
 IR: 1682, 815 cm^{-1}
39. $^1\text{H-NMR}$: δ/ppm 2.4 (s, 3H), 3.9 (s, 3H), 7.17 (m, 1H), 7.18 (m, 1H), 7.35 (m, 1H), 7.85 (m, 1H)
 $^{13}\text{C-NMR}$: δ/ppm 14.1, 50.0, 125.4, 129.1, 129.6, 131.2, 132.7, 138.9, 167.0
 IR: 1723, 1260, 736 cm^{-1}
40. $^1\text{H-NMR}$: δ/ppm 2.4 (s, 3H), 7.3 (d, 2H), 7.9 (d, 2H), 12.8 (s, 1H, D_2O exchange)
 $^{13}\text{C-NMR}$: δ/ppm 21.1, 128.1, 129.1, 129.4, 143.0, 167.3
 IR: 3500, 1680, 1287 cm^{-1}
41. $^1\text{H-NMR}$: δ/ppm 2.3 (s, 3H), 3.7 (s, 3H), 6.8 (d, 2H), 7.05 (d, 2H)
 $^{13}\text{C-NMR}$: δ/ppm 20.4, 55.2, 113.6, 113.8, 129.9, 157.7
 IR: 1249, 818 cm^{-1}

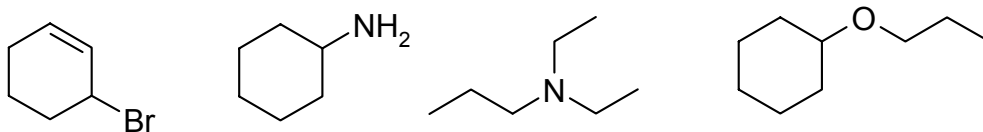
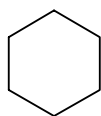


6% PART 6: SYNTHESIS

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

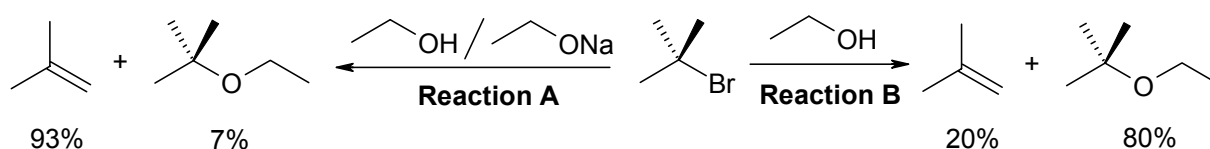
WRITE YOUR ANSWERS IN THE BOOKLET PROVIDED.

DO NOT SHOW MECHANISMS.

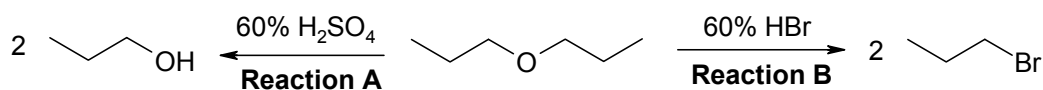
TARGETS**Allowed Starting Materials:**

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

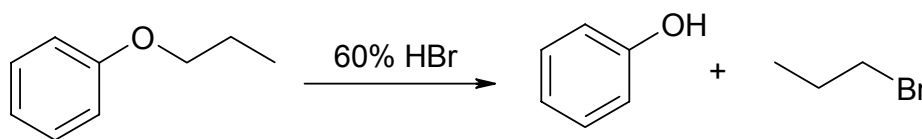
In addition you may use any solvents and /or inorganic reagents required.

9% 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.**

- For **reaction A**, propose a mechanism for the formation of 2-methylpropene.
- For **reaction B**, propose a mechanism for the formation of the ether.
- Explain briefly the reason for the difference in product ratio for the **reactions A** and **B**

OR**II.**

- For **reaction A**, propose a mechanism for the formation of 1-propanol.
- For **reaction B**, propose a mechanism for the formation of 1-bromopropane.
- Explain briefly why the following reaction leads to one alcohol (phenol) and one alkyl halide (1-bromopropane) and not two halides.

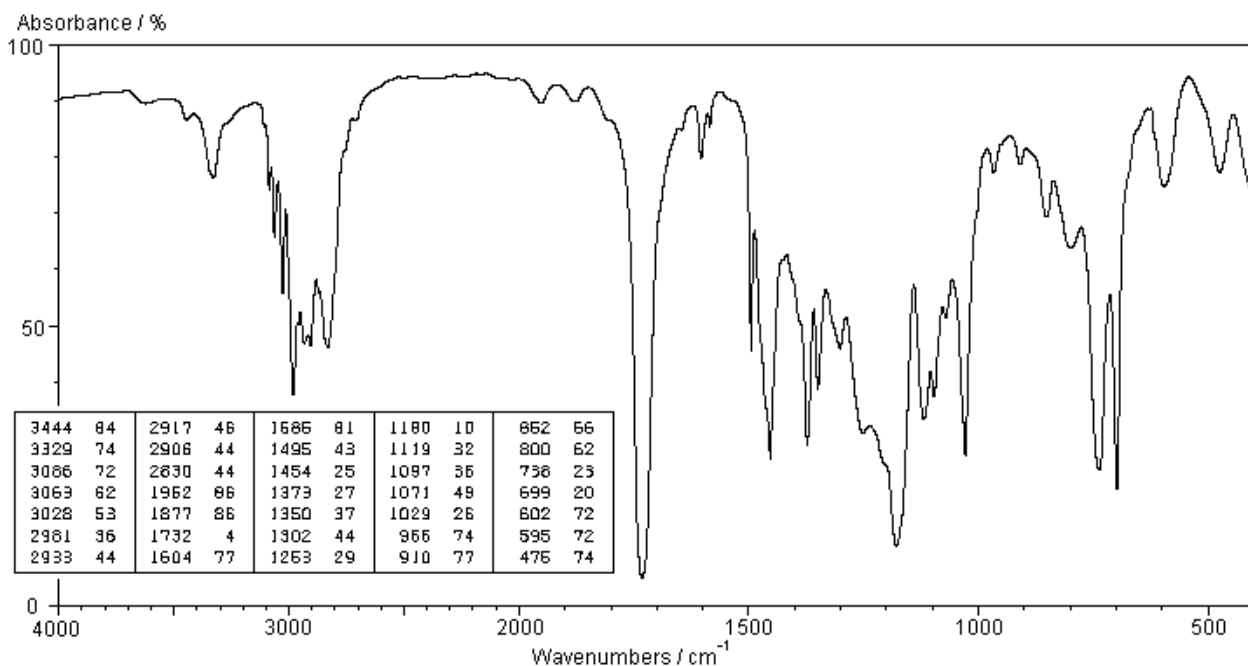
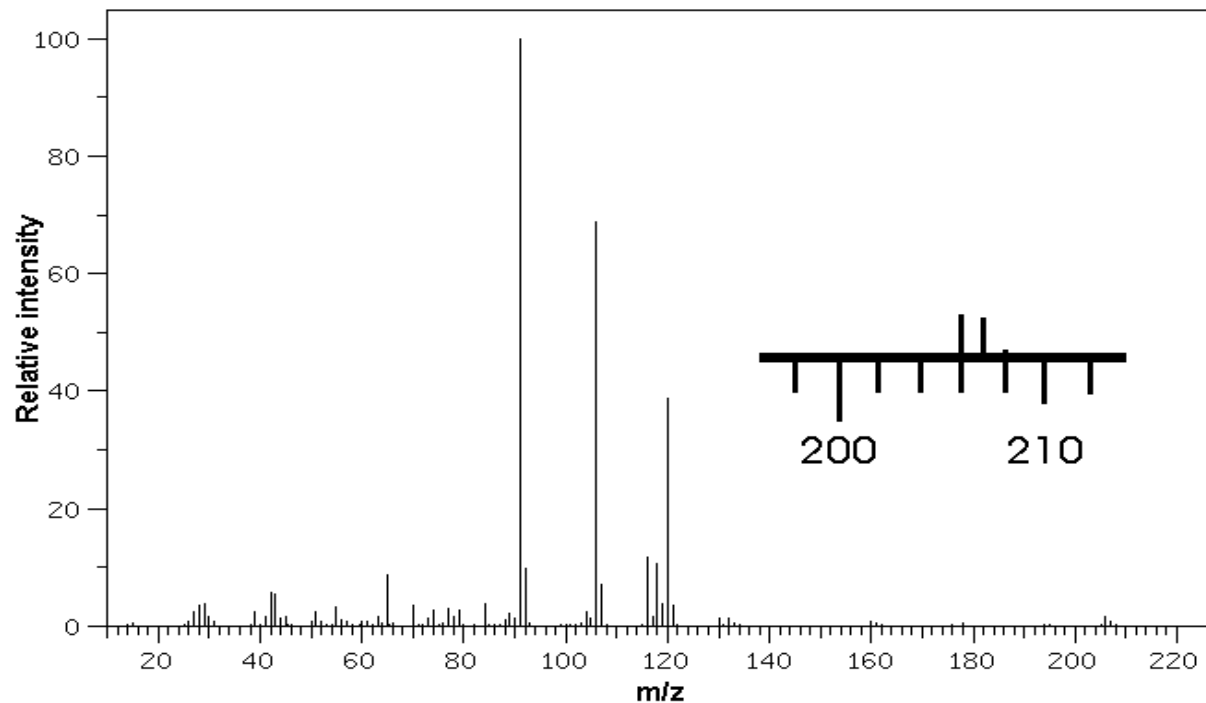


10% PART 8: SPECTROSCOPY

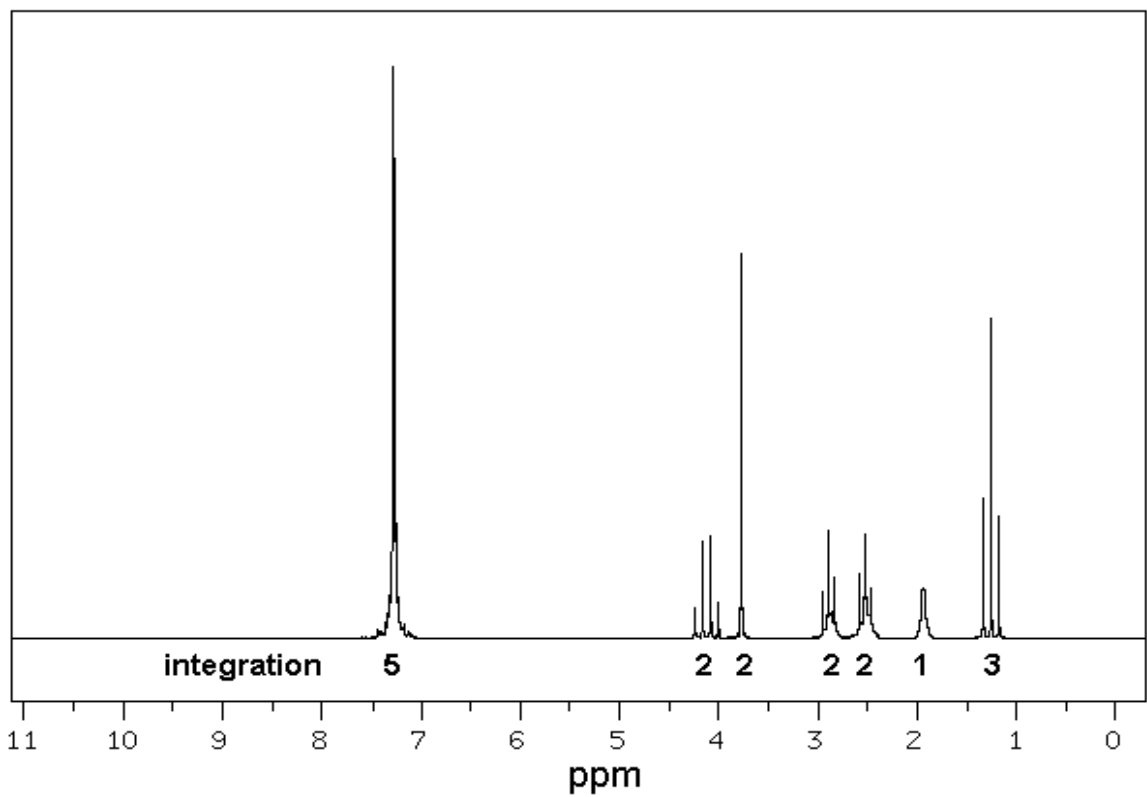
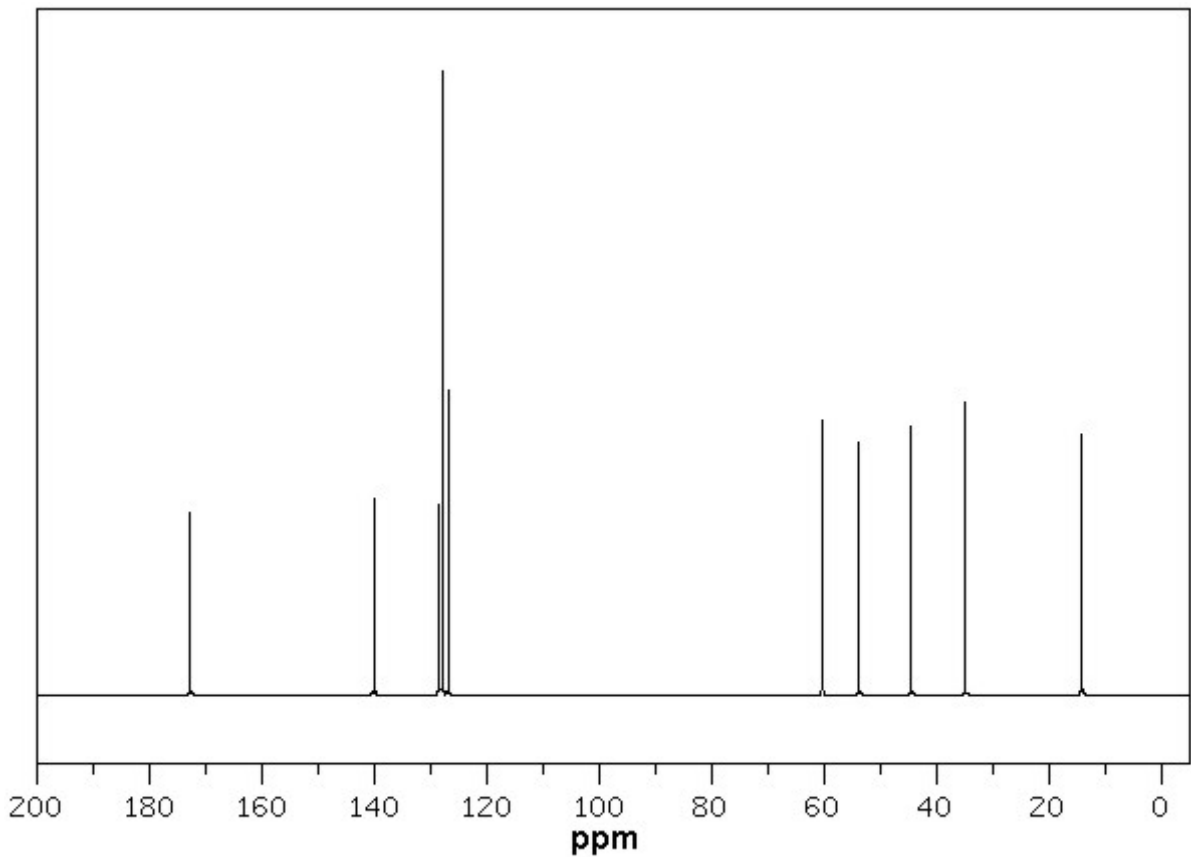
WRITE YOUR ANSWERS IN THE BOOKLET PROVIDED. Show your workings as PARTIAL marks will be given.

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

Elemental analysis for C, H and N only : 69.54% C, 8.27% H and 6.76% N



Cont'd -->



12% PART 9: STRUCTURE DETERMINATION**WRITE YOUR ANSWERS IN THE BOOKLET PROVIDED**

An achiral hydrocarbon **A**, C_6H_{12} , was reacted with bromine / UV light to give **B** as the major product. **B** was found to react quickly with $AgNO_3$ / ethanol and slowly with NaI in acetone.

When **B** was heated with $KOtBu$ in $tBuOH$ it gave **C** as the major product. **C** reacted with Br_2 / $CHCl_3$ to give a colourless solution.

Reaction of **B** with aq. Na_2CO_3 solution gave **D** (IR: 3500 cm^{-1} , broad). Heating **D** with conc. sulfuric acid gave 1-methylcyclopentene as the major product, which is a constitutional isomer of **C**,

Reaction of **D** with PCl_3 / Et_3N gave **E**.

Reaction of **A** with Cl_2 / UV light gave a mixture of four constitutional isomers **E**, **F**, **G**, and **H** in relative yields $G = H > E > F$. Of these four isomers, only **G** and **H** were chiral. The ^{13}C -nmr spectrum of **A**, **E** and **F** each had four signals whereas **G** and **H** had six. In the 1H -nmr spectrum of **G** the most deshielded peak is a quartet (1 H) whereas the most deshielded peak in **H** is a quintet (1 H).

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

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