THE UNIVERSITY OF CALGARY

FACULTY OF SCIENCE

MIDTERM EXAMINATION

CHEMISTRY 353

FEBRUARY 27th, 2002 Time: 2 Hours

PLEASE WRITE YOUR NAME, STUDENT I.D. NUMBER AND SECTION NUMBER (01 for MWF lectures and 02 for TR lectures) **ON YOUR COMPUTER ANSWER SHEET** and in the **ANSWER BOOKLET** provided.

READ THE INSTRUCTIONS CAREFULLY

The exam consists of Parts 1 - 8, each of which should be attempted. Note that some Parts provide you with a choice of questions, e.g. 5 out of 6. 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, 7 and 8 are to be answered **IN THE BOOKLET PROVIDED**. A periodic table with atomic numbers and atomic weights and spectroscopic data tables are appended.

Parts 1 - 5 consist of a series of multiple choice questions numbered 1 - 32 which are to be answered on the 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

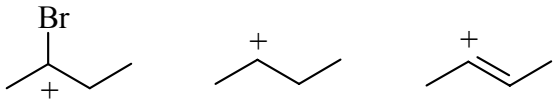
15% **ANSWER ANY FIVE (5) OF QUESTIONS 1-8**.

Arrange the items in the questions in this section in **DECREASING ORDER** (greatest 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:

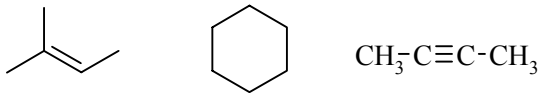


i **ii** **iii**

2. The relative yields of the following alkyl bromides from the reaction of 2-methylbutane with Br_2 / uv light:

i 1-bromo-2-methylbutane
ii 2-bromo-2-methylbutane
iii 2-bromo-3-methylbutane

3. The relative reactivity of each of the following towards aq. H_2SO_4:



i **ii** **iii**

4. The relative reactivity of each of the following towards *trans*-2-butene:

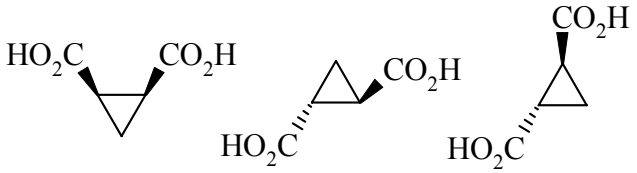
HCl HBr H_2O

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 specific rotation of the following molecules given that (S,S)-cyclopropane-1,2-dicarboxylic acid has a specific rotation = -84^o and concentration = 1g/ml and path length = 10cm:

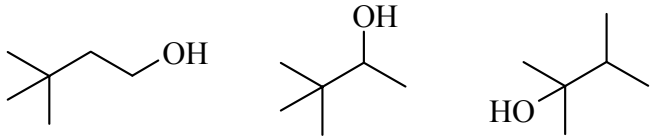


i **ii** **iii**

6. The relative reactivity towards H_2 / Pd of the following:

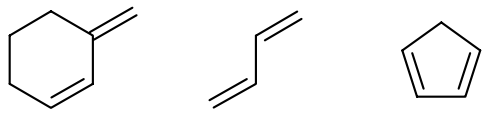
i **ii** **iii**

7. The relative yields of the following products from the reaction of 3,3-dimethyl-1-butene with BH_3 followed by the normal work-up with NaOH / H_2O_2 :



i **ii** **iii**

8. The relative reactivity towards acrylonitrile (or cyanoethene) of each of the following:



i **ii** **iii**

PART 2: LABORATORY

11% **ANSWER ALL FIVE (5) OF THE QUESTIONS 9-13.**

Questions 9-13 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.

9. From the experiment about the hydrolysis of sucrose, which of the following statements are true ?

   A sucrose is a disaccharide of glucose and fructose.

   B specific rotation $[\alpha]_D = \alpha.c.l$ (where α = observed rotation, c = concentration in g /ml and l = cell pathlength in dm).

   C the hydrolysis reaction is acid catalysed.

   D the pKa of hydrochloric acid is about 5.

   E an anomeric carbon is characterised by having two oxygen atoms attached by single bonds.

10. From the experiment about the chemistry of milk, which of the following statements are true ?

   A the main sugar in milk is galactose.

   B casein is an example of a protein.

   C Benedicts solution gives a yellow precipitate in the presence of a reducing sugar.

   D the white precipitate formed when acid is added to milk is mainly lactose.

   E ninhydrin stains all amino acids as blue to purple spots when used to develop the chromatogram.

11. From the experiment about the isolation of natural products, which of the following statements are true ?

   A steam distillation is controlled by the same law, Raoult's law, as simple distillation.

   B steam distillation allows volatile materials to be distilled below their normal boiling point.

   C organic solutions can be dried with anhydrous sodium sulfate.

   D in an extraction using a separatory funnel the organic layer will always be the bottom layer.

   E infra red spectroscopy is used to deduce the connectivity of the hydrocarbon skeleton.

12. From the experiment about lipids, soaps and detergents, which of the following statements are true ?

A the more saturated a fat or oil, then the higher its melting point.

B a more unsaturated fat has more C=C units.

C oleic acid has the molecular formula $C_{18}H_{34}O_2$.

D esters are hydrolysed to give carboxylic acids and alcohols.

E the precipitate formed when H_2SO_4 is added to an aqueous soap solution is Na_2SO_4.

13. From the laboratory in general, which of the following statements are true ?

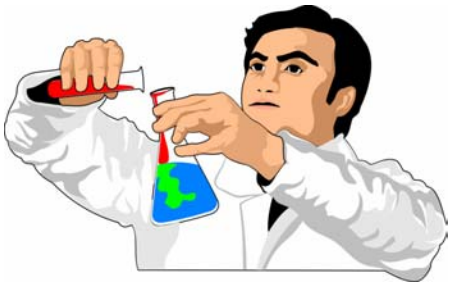
A a Buchner funnel is used for vacuum filtrations.

B a reflux apparatus is used to separate a mixture of liquids with different boiling points.

C charcoal is used to remove residual water from organic solutions.

D aqueous waste should be disposed of by washing it down the sink with water.

E the person below is suitably equipped for an experiment.

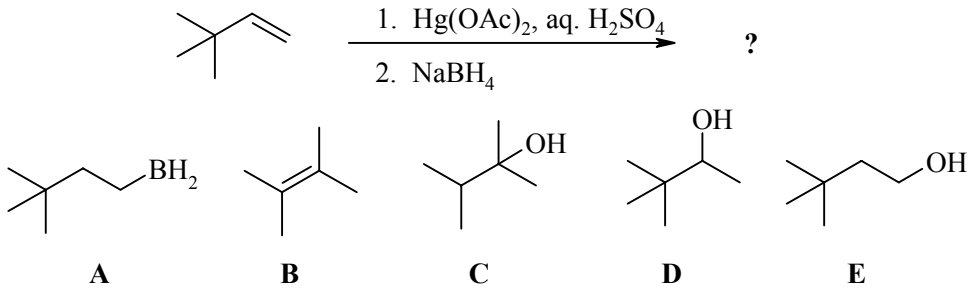


PART 3: STARTING MATERIALS AND PRODUCTS OF REACTIONS

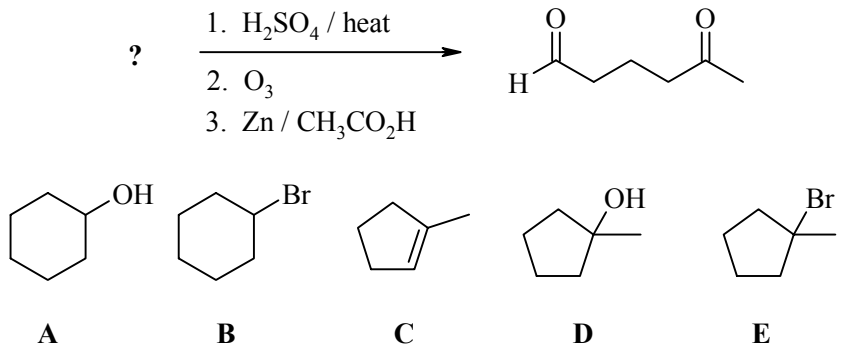
15% **ANSWER ANY SIX (6) OF QUESTIONS 14-20.**

For each of questions **14-20** select either the major product or the starting material required in order to complete of the reaction schemes.

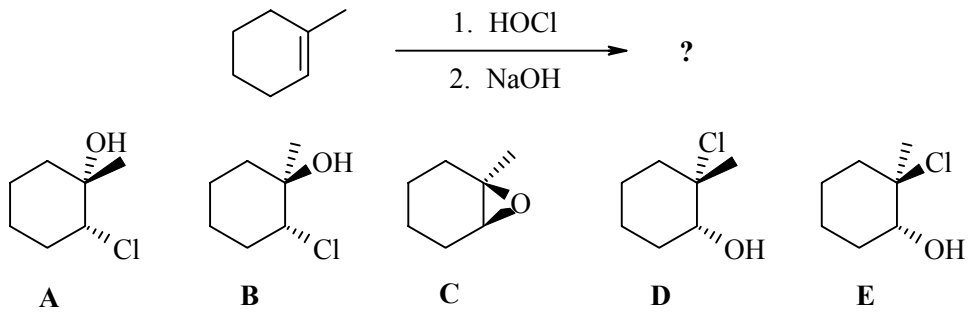
14.



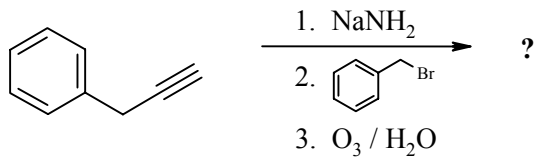
15.

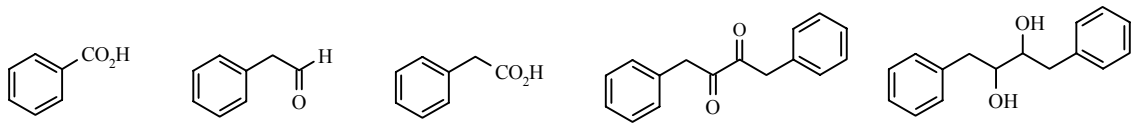


16.



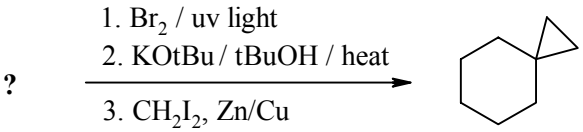
17.

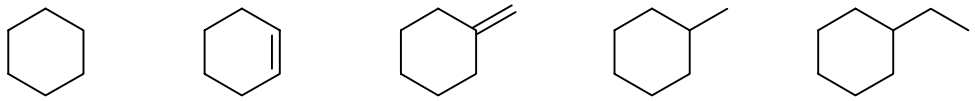




A **B** **C** **D** **E**

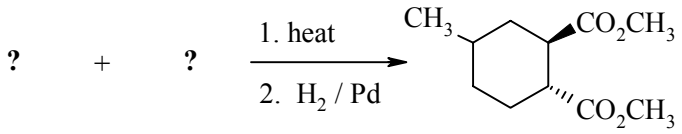
18.



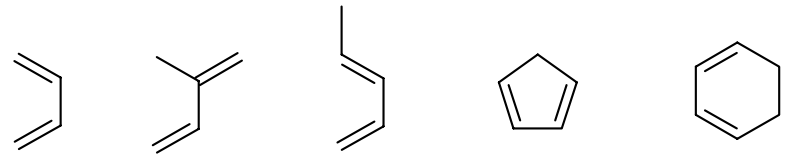


A **B** **C** **D** **E**

The last two questions **both apply** to the following reaction scheme:

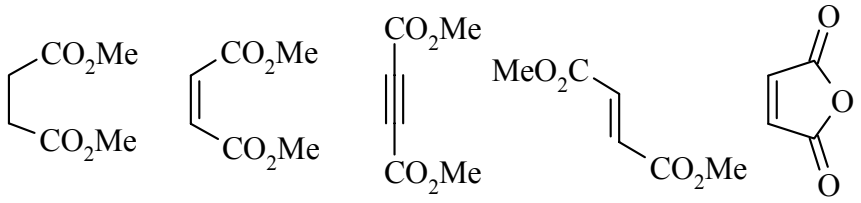


19.



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

20.



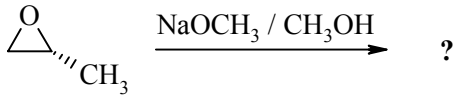
A. **B.** **C.** **D.** **E.**

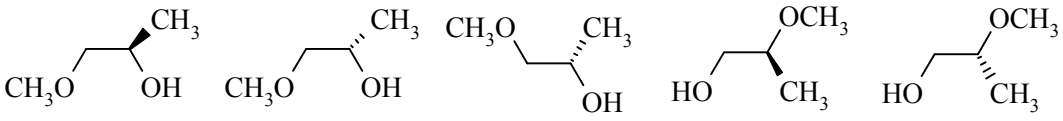
PART 4: REGIO- and STEREOCHEMISTRY OF REACTIONS

15% **ANSWER ANY FIVE (5) OF QUESTIONS 21-26**.

For each of the questions **21-26**, select the structure required to complete the reaction shown. If two products are equally abundant, then you must indicate **both** for full marks. If two starting materials will give the same product, then you must indicate **both** for full marks. In order to indicate more than one structure, blacken the spaces corresponding to each one.

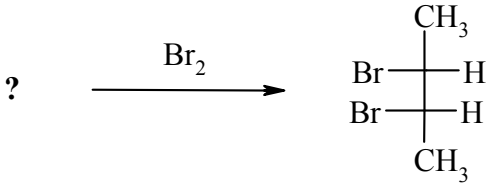
21.

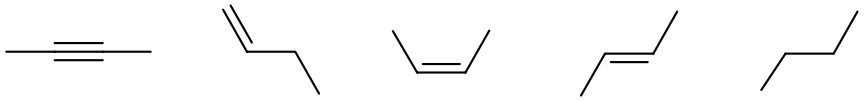




A **B** **C** **D** **E**

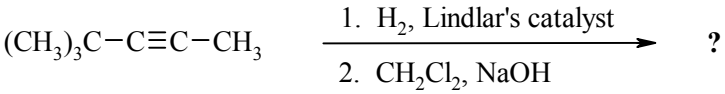
22.

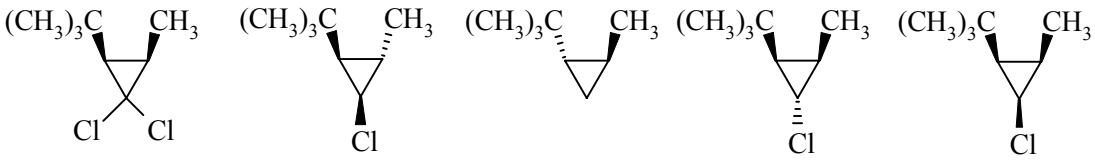




A **B** **C** **D** **E**

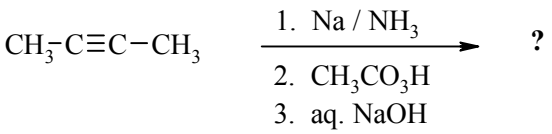
23.

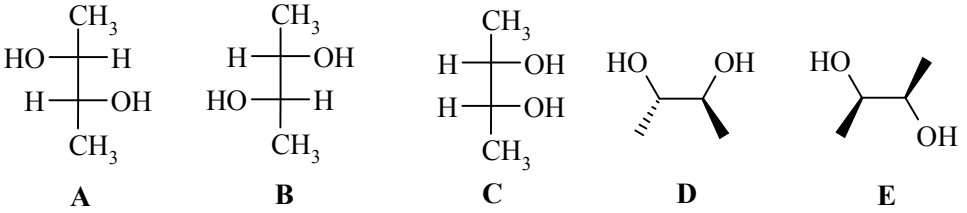




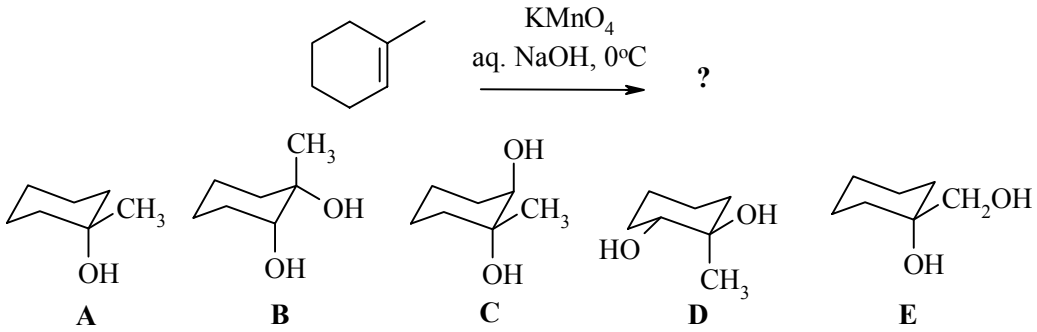
A **B** **C** **D** **E**

24.

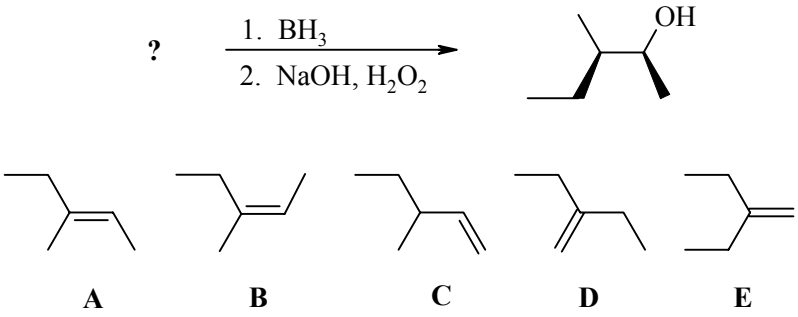

CH3–C≡C–CH3
1. Na / NH3
2. CH3CO3H
3. aq. NaOH
?


A
B
C
D
E

25.


KMnO4
aq. NaOH, 0°C
?
A
B
C
D
E

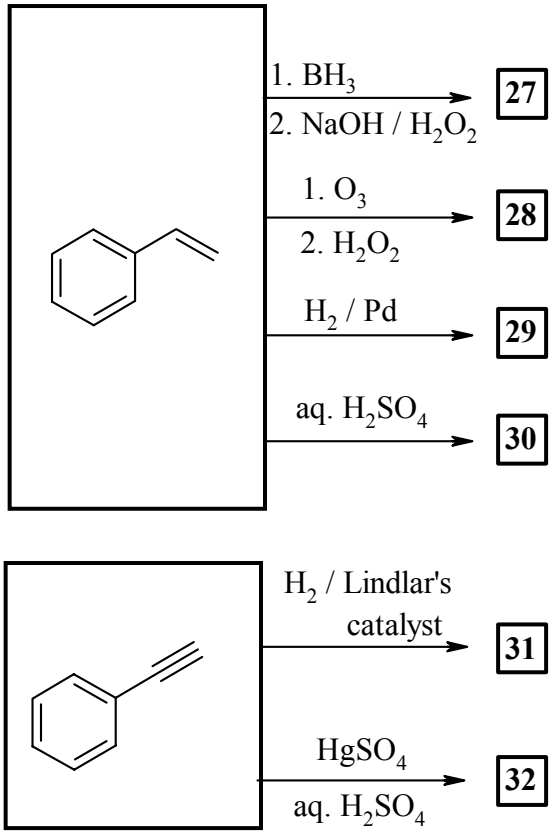
26.

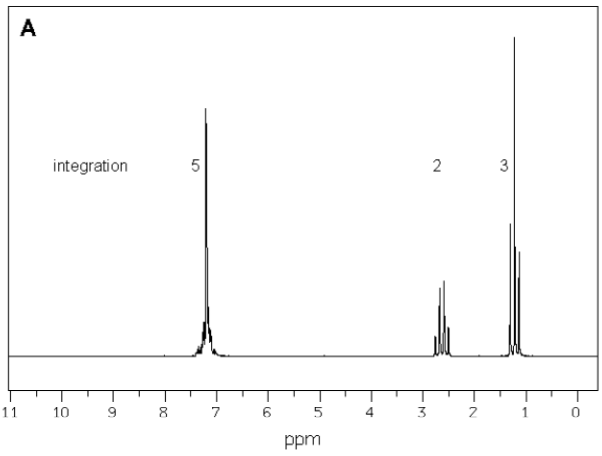

?
1. BH3
2. NaOH, H2O2
A
B
C
D
E

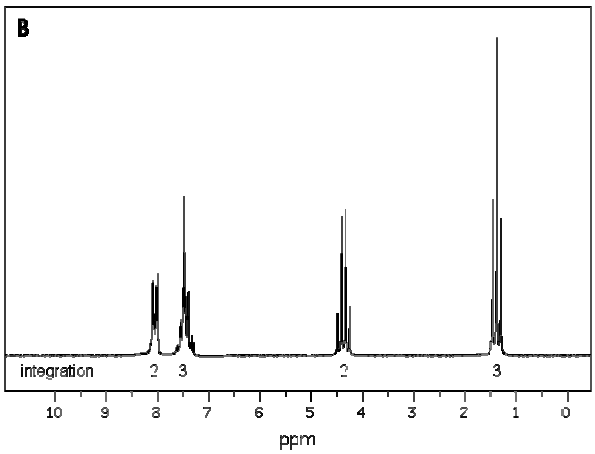
PART 5: APPLIED SPECTROSCOPY

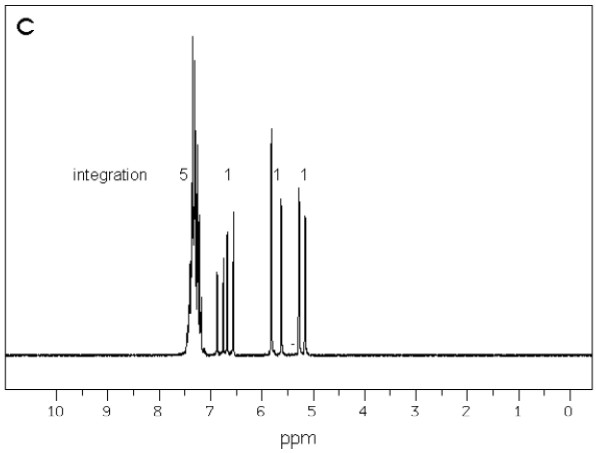
10% **ANSWER ANY FIVE (5) OF QUESTIONS 27-32**.

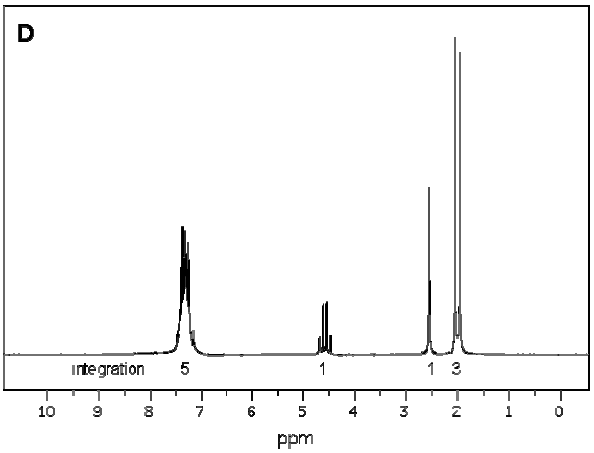
A novice organic chemist was carrying out the sequence of reactions shown below. However, they managed to mix up all of the ^{1}H-NMR spectra ! Each of the **BOXED NUMBERS** in the scheme indicates a compound, for each compound select from the ^{1}H-NMR spectra provided the spectra that corresponds to that compound:

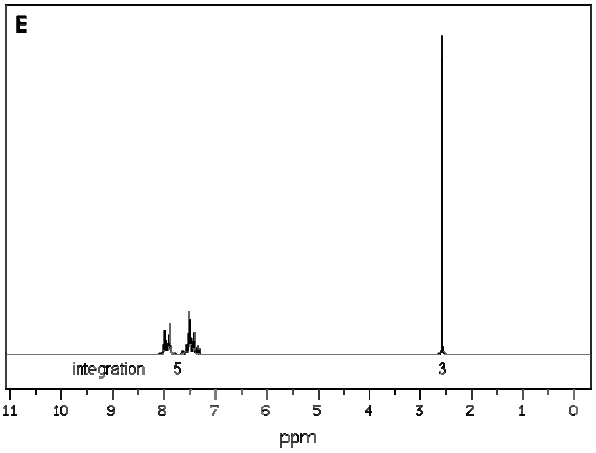


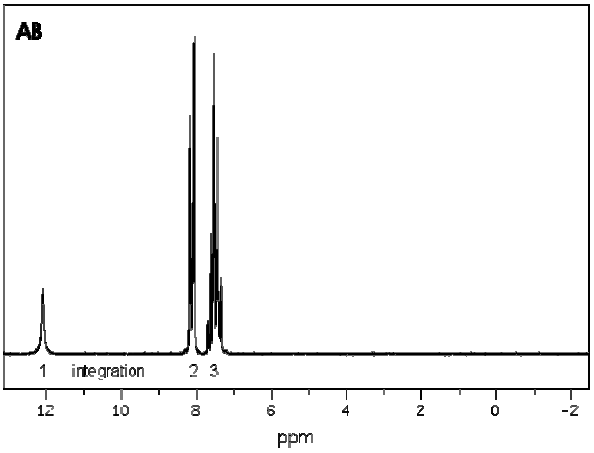

A
integration 5 2 3
11 10 9 8 7 6 5 4 3 2 1 0
ppm

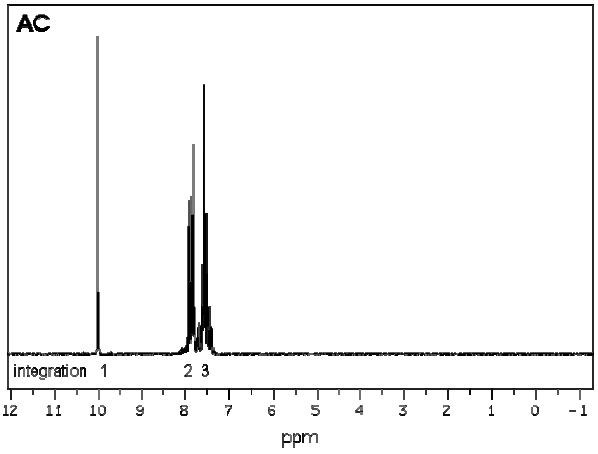

B
integration 2 3 2 3
10 9 8 7 6 5 4 3 2 1 0
ppm

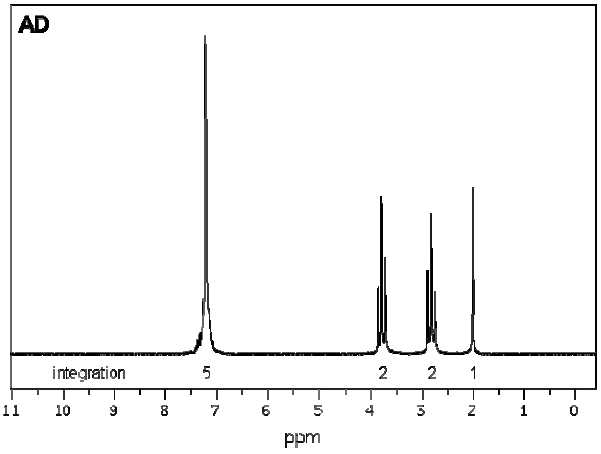

C
integration 5 1 1 1
10 9 8 7 6 5 4 3 2 1 0
ppm


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


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


AB
1 integration 2 3
12 10 8 6 4 2 0 -2
ppm


AC
integration 1 2 3
12 11 10 9 8 7 6 5 4 3 2 1 0 -1
ppm


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

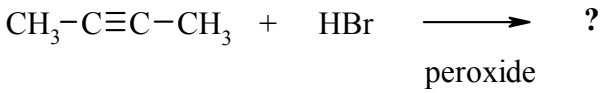
PART 6: MECHANISMS

10% **ANSWER ANY TWO (2) OF QUESTIONS A - C**

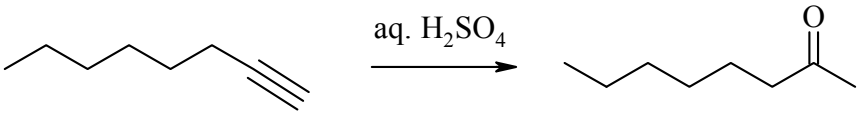
WRITE YOUR ANSWER IN THE BOOKLET PROVIDED

Use curly arrow mechanisms to answer TWO (2) of the following questions:

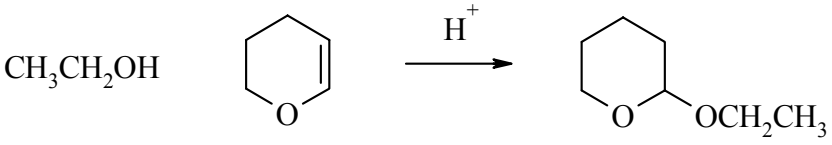
A. Use your knowledge of the reaction of alkenes with HBr and peroxides (or uv light) and of alkynes with HBr (dark / N_2 atmosphere) to predict the outcome of the following reaction (assume excess HBr):



B Show the mechanism for the following transformation:



C Use your knowledge of the reaction of alkenes with aqueous acid to suggest a mechanism for the following transformation (make sure you justify the regiochemistry):



PART 7 : STRUCTURE DETERMINATION

12% **WRITE YOUR ANSWER IN THE BOOKLET PROVIDED**

Compound **A** is a hydrocarbon with analysis 83.23 %C, 16.77 %H by weight. When **A** was reacted with bromine / uv light, four different monobromination products were obtained of which **B** was by far the most abundant. **B** was found to react rapidly with $AgNO_3$ / aqueous ethanol but very slowly with NaI / acetone. When **B** was heated with KOH / ethanol, a mixture of two isomeric products **C** and **D** was generated, with **C** being the major product.

The mixture of **C** and **D** was treated with ozone in methanol followed by a work-up with zinc in acetic acid. This produced a mixture of four compounds : methanal, ethanal, 2-propanone and 2-butanone.

Compound **C** was isolated from the original mixture and was treated with bromine in chloroform to give **E**. When **E** heated with KOH / ethanol gave **F**. A sample of **F** was heated in a sealed tube at 250^{o}C and a mixture of four isomeric products was obtained. One of these products, **G**, $C_{10}H_{16}$, was isolated and subjected to ozonolysis followed by work-up with hydrogen peroxide. A gas was evolved during the work-up and only a single product was isolated, 3-(1-oxoethyl)-6-oxoheptanoic acid (also known as 3-acetyl-6-oxoheptanoic acid. Catalytic reduction of **G** using excess hydrogen over a palladium catalyst gave 1-methyl-4-(1-methylethyl)cyclohexane (also known as 1-isopropyl-4-methylcyclohexane).

Catalytic hydrogenation under the same conditions of **C**, **D** and **F**, all gave the original hydrocarbon **A**.
Of the compounds described, only **E** and **G** were chiral.

- Identify **A** - **G**.

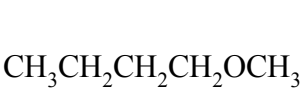
- Show the curly arrow mechanism for the formation of **G** from **F**.

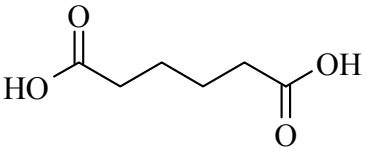
PART 8: SYNTHESIS

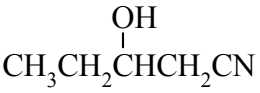
12% Using any of the starting materials shown, design efficient syntheses of any **THREE (3)** of the following molecules.

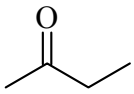
WRITE YOUR ANSWERS IN THE BOOKLET PROVIDED.

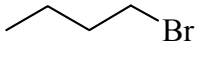
DO NOT SHOW MECHANISMS

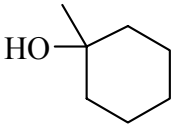


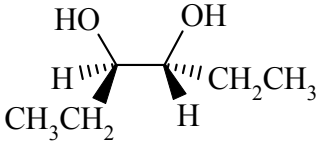


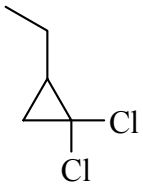




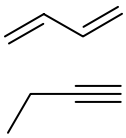








Allowed Starting Materials:



any inorganic reagents
any other compounds with 3 or less C atoms