

THE UNIVERSITY OF CALGARY

FACULTY OF SCIENCE

MIDTERM EXAMINATION

CHEMISTRY 353

FEBRUARY 25th, 2003

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 (inside front cover) and spectroscopic data tables are included with this examination paper.

Parts 1 - 5 consist of a series of multiple choice questions numbered 1 - 34 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**.

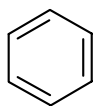
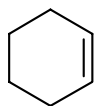
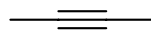
PART 1: RELATIVE PROPERTIES**12% ANSWER ANY SIX (6) OF QUESTIONS 1-8.**

Arrange the items in the questions in this section in **DECREASING ORDER** (i.e. greatest first) with respect to the indicated property.

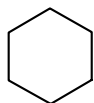
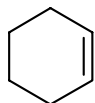
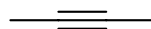
Use the following code to indicate your answers.

- | | | | |
|-----------|---------------------------|------------|---------------------------|
| A. | i > ii > iii | D. | ii > iii > i |
| B. | i > iii > ii | E. | iii > i > ii |
| C. | ii > i > iii | AB. | iii > ii > i |

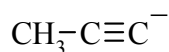
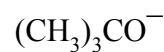
1. The relative reactivity of the following towards H₂ with a Pd catalyst :

**i****ii****iii**

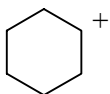
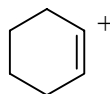
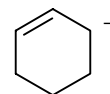
2. The relative reactivity of the following towards HBr (dark, N₂ atmosphere) :

**i****ii****iii**

3. The relative basicity of each of the following:

**i****ii****iii**

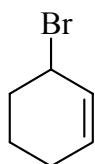
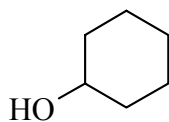
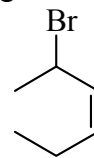
4. The relative stability of the following carbocations:

**i****ii****iii**

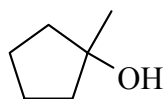
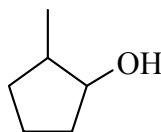
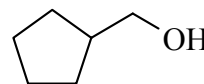
Use the following code to indicate your answers.

- | | | | |
|-----------|---------------------------|------------|---------------------------|
| 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 stereoisomers of each of the following:

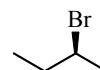
**i****ii****iii**


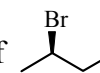
6. The relative yields of the following products from the reaction of 1-methylcyclopentene with BH_3 followed by the normal work-up with aq. $\text{NaOH} / \text{H}_2\text{O}_2$:

**i****ii****iii**

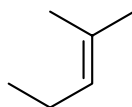
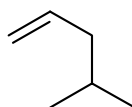
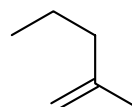
7. The observed rotation for each of the following solutions given that (S)-2-bromobutane has a specific rotation = $+23.1^\circ$ and that the same polarimetry cell is used for each measurement.

i 2g of  in 20ml of EtOH

ii 1.5g of  in 30ml of EtOH

iii 1g of  and 2g of  in 20ml of EtOH

8. The relative heats of hydrogenation of the following alkenes (most exothermic to least exothermic) :

**i****ii****iii**

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PART 2: LABORATORY

12% 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 an example of a monosaccharide.
 - 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 molecular formula of sucrose is $C_{12}H_{22}O_{11}$.
 - D the pKa of hydrochloric acid is about 7.
 - E an acetal is formed by the reaction between an acid and an alcohol.
10. From the experiment about the chemistry of milk, which of the following statements are true ?
- A lactose is isomeric with sucrose.
 - B proteins can be hydrolysed to amino acids using aqueous acid.
 - C Benedict's solution is alkali copper (II) sulfate.
 - D the most abundant amino acid in casein is cystine acid.
 - E in general the less polar the amino acid, the lower the R_f on the paper chromatogram.
11. From the experiment about the isolation of natural products, which of the following statements are true ?
- A terpenes are a common class of natural products.
 - B steam distillation relies on the formation of hydrates to lower the boiling point.
 - C anhydrous sodium sulfate can be used to remove residual water.
 - D in extraction using a separatory funnel the aqueous layer will always be the top layer regardless of which organic solvent is used.
 - E infra-red spectroscopy can be used to detect the functional groups in the natural product.

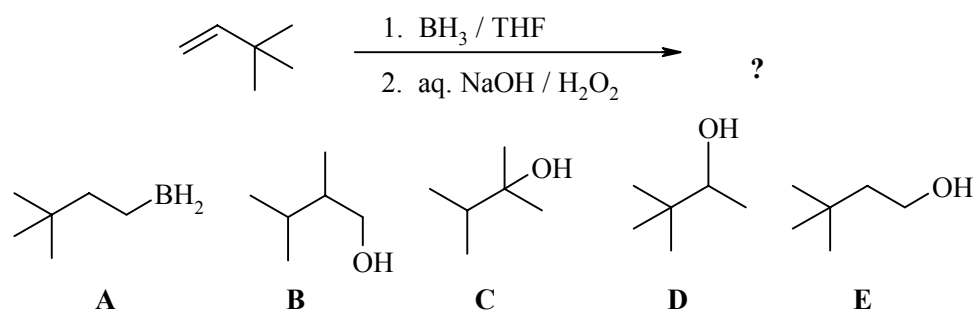
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12. From the experiment about polymers, which of the following statements are true ?
- A** when condensation polymers are formed, a small molecule such as water is a by-product
 - B** cross-linking makes a polymer more flexible.
 - C** Kevlar is an example of a polyester.
 - D** esters are hydrolysed to give carboxylic acids and alcohols.
 - E** one of the by-products in PETE depolymerisation is glycerol.
13. From the laboratory in general, which of the following statements are true ?
- A** a Buchner funnel can be used for separations of immiscible liquids.
 - B** boiling chips are used to increase the boiling point of a liquid.
 - C** filtration is used to separate solids from liquids or solutions.
 - D** aqueous waste should be disposed of by washing it down the sink with water.
 - E** a condenser in a "reflux" position prevents solvent vapours from escaping a reaction vessel.

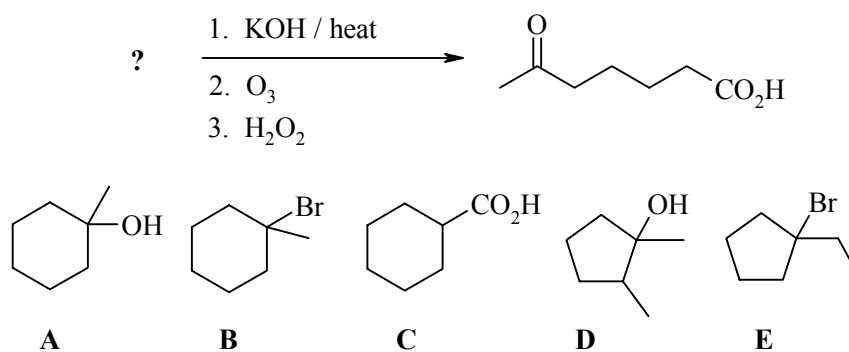
PART 3: STARTING MATERIALS AND PRODUCTS OF REACTIONS**15% ANSWER ANY SIX (6) OF QUESTIONS 14-20.**

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

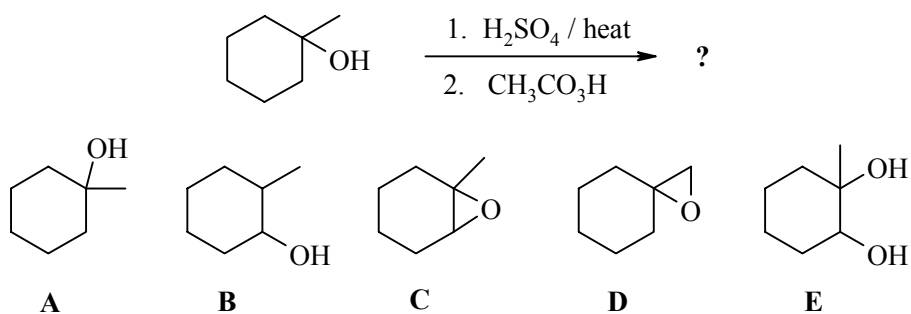
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15.

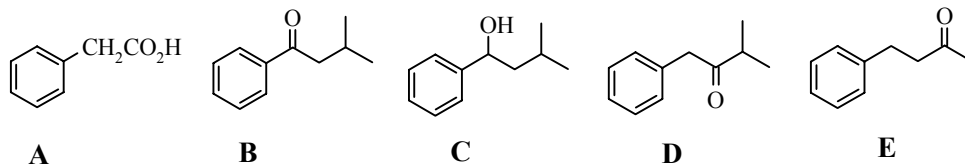
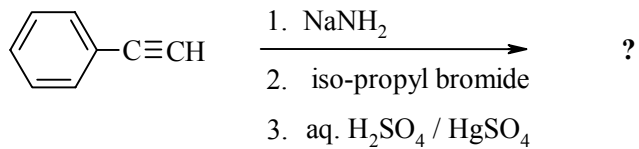


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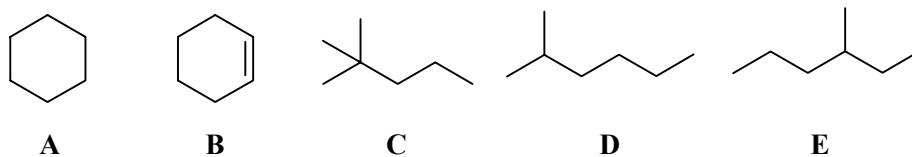
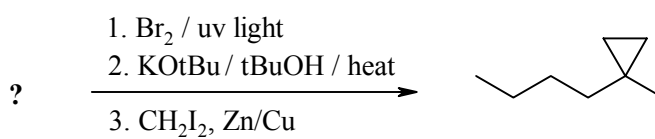


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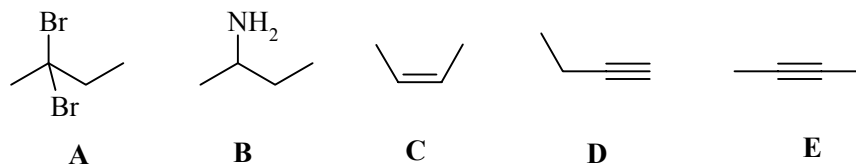
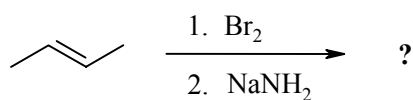
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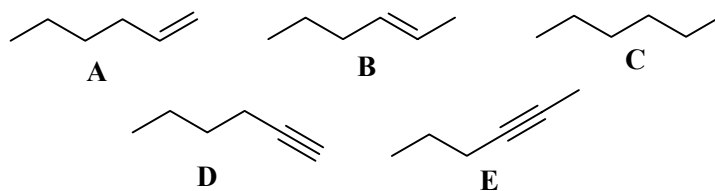
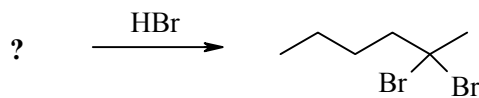
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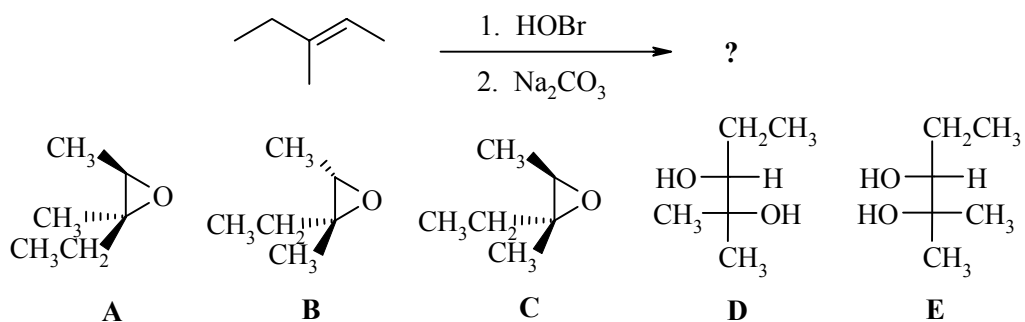
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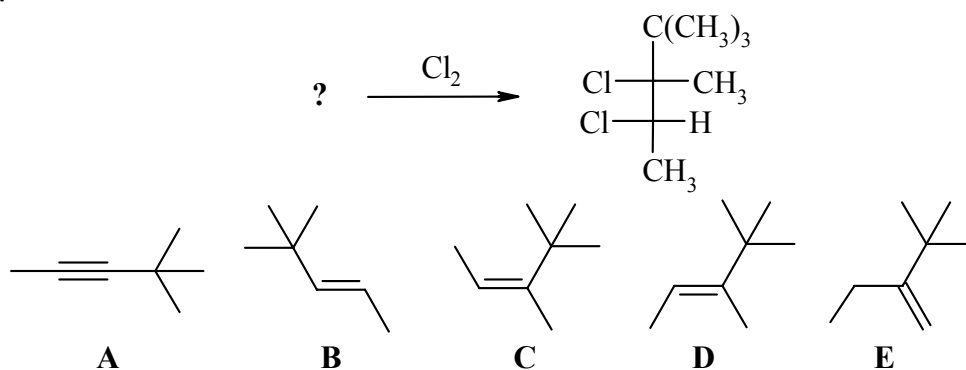
PART 4: REGIO- and STEREOCHEMISTRY OF REACTIONS**15% ANSWER ANY FIVE (5) OF QUESTIONS 21-26.**

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.

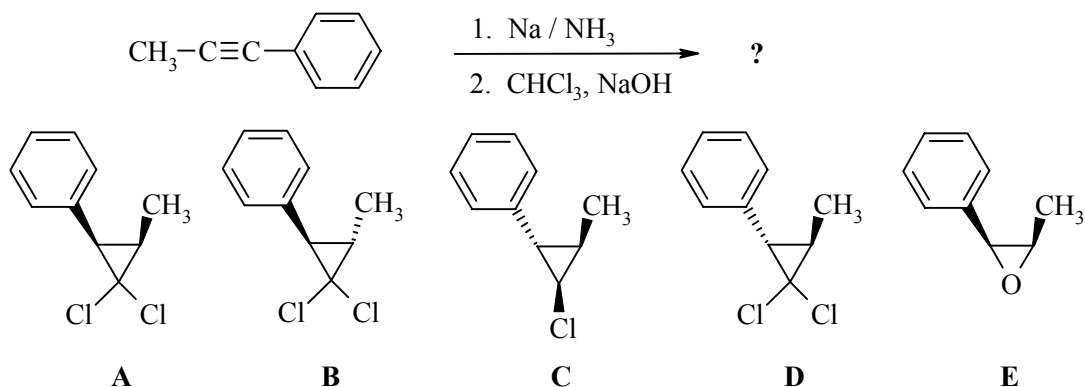
21.



22.

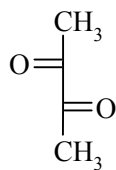
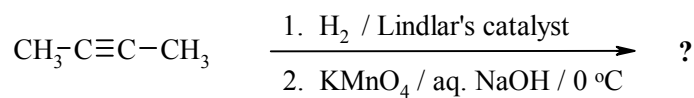
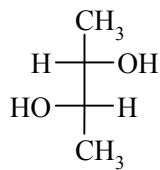
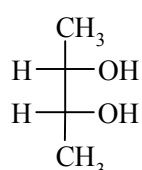
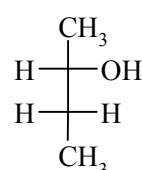
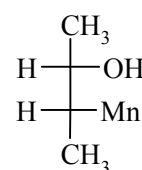


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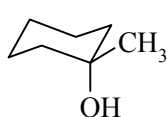
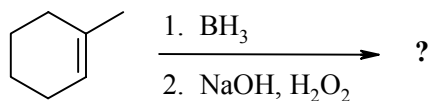
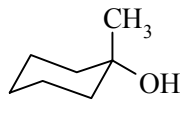
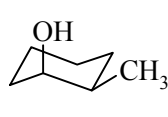
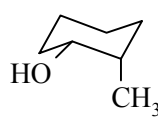
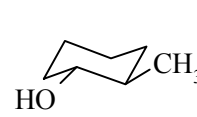


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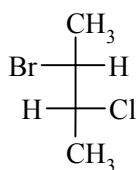
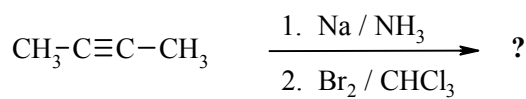
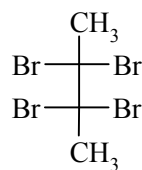
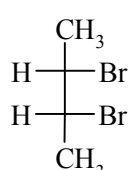
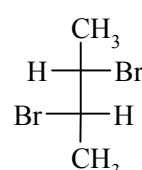
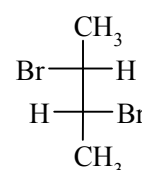
24.

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

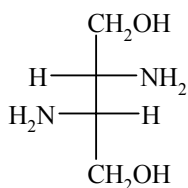
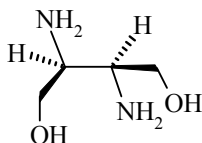
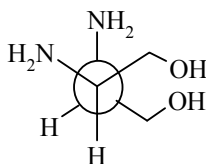
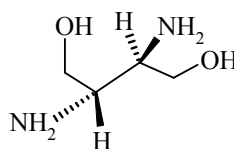
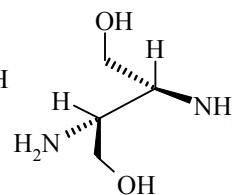
25.

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

26.

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

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PART 5 : STEREOCHEMISTRY**12% ANSWER ALL EIGHT (8) of the questions 27 to 34.**Use the structures **A-E** of 2,3-diamino-1,4-butandiol shown below to answer questions **27-34****A.****B.****C.****D.****E.**

27. Choose **TWO** conformational isomers.
28. Choose **TWO** enantiomers.
29. Choose **TWO** diastereomers.
30. Choose **ALL** meso compounds.
31. Choose **ALL** structures that represent an eclipsed conformation.

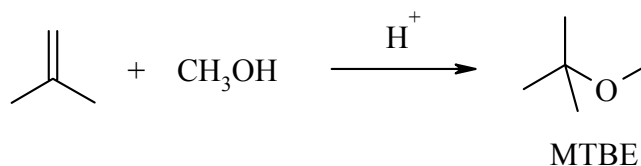
A solution containing 1.2 g of **A** and 0.3 g of **B** in 10 ml of ethanol was placed in a 1 dm cell and the optical rotation measured in a polarimeter. The observed rotation was $+5.1^\circ$.

32. What is the specific rotation of the mixture?
- A.** $+3.4^\circ$ **B.** $+7.65^\circ$ **C.** $+76.5^\circ$ **D.** -7.65° **E.** $+34^\circ$
33. What is the specific rotation of (R,R)- 2,3-diamino-1,4-butandiol ?
- A.** $+70.8^\circ$ **B.** -70.8° **C.** $+56.67^\circ$ **D.** -56.67° **E.** $+76.5^\circ$ **AB.** -76.5°
34. What is the % optical purity or enantiomeric excess (ee) of this mixture of **A** and **B**?
- A.** 20 **B.** 40 **C.** 50 **D.** 60 **E.** 75

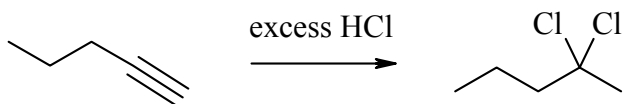
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PART 6: MECHANISMS**10% ANSWER ANY TWO (2) OF QUESTIONS A - C****WRITE YOUR ANSWER IN THE BOOKLET PROVIDED****Use curly arrow mechanisms to answer each of the following questions. NO other reagents are required.**

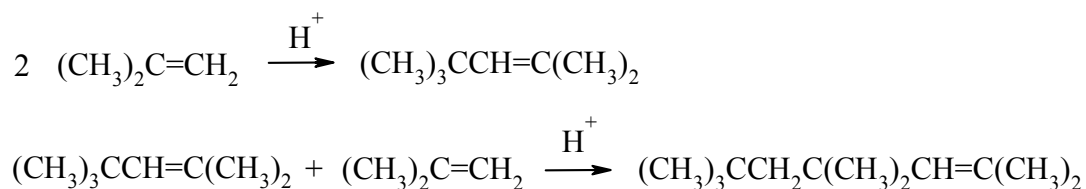
- A.** Methyl t-butyl ether, also known as MTBE, is a controversial gasoline additive made from methanol and 2-methylpropene. Show the mechanism for the following transformation that is used to synthesise MTBE :



- B** Show the mechanism for the following transformation and rationalise the regiochemistry :



- C** Show the mechanism for the following polymerisation reaction :



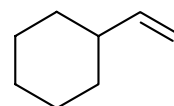
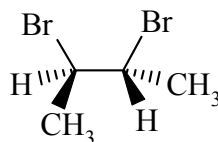
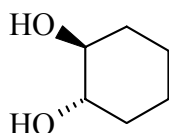
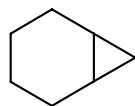
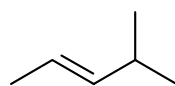
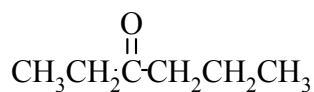
CONTINUED -->

PART 7 : SYNTHESIS

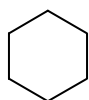
12% Using any of the starting materials shown, design efficient syntheses of any **THREE (3)** of the following molecules.

WRITE YOUR ANSWERS IN THE BOOKLET PROVIDED.

DO NOT SHOW MECHANISMS.



Allowed Starting Materials:

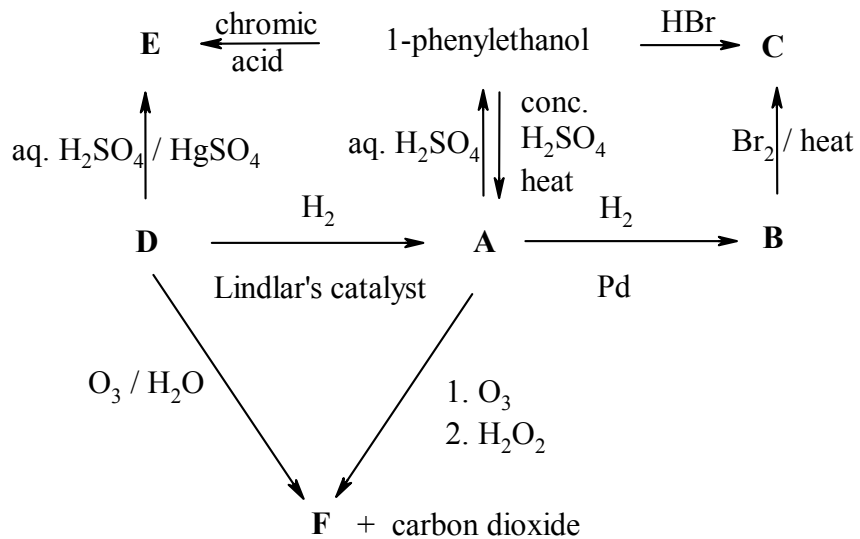


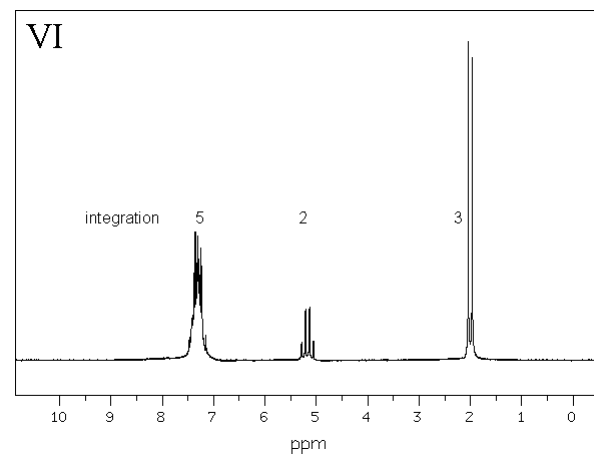
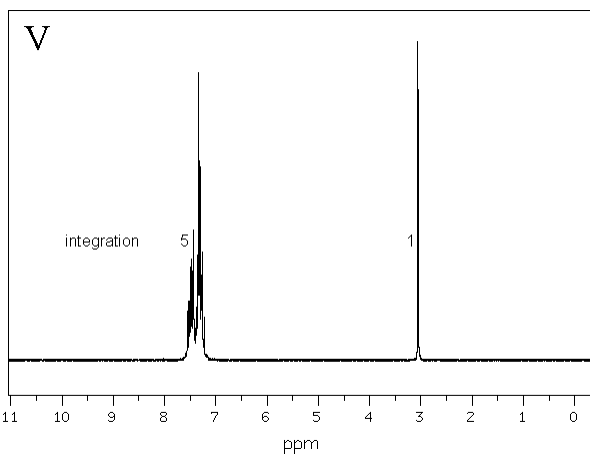
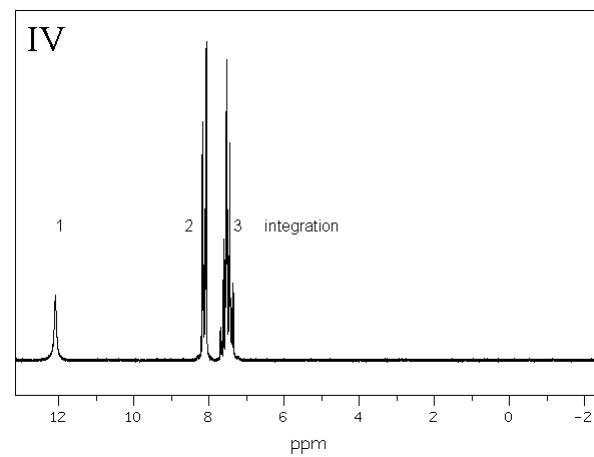
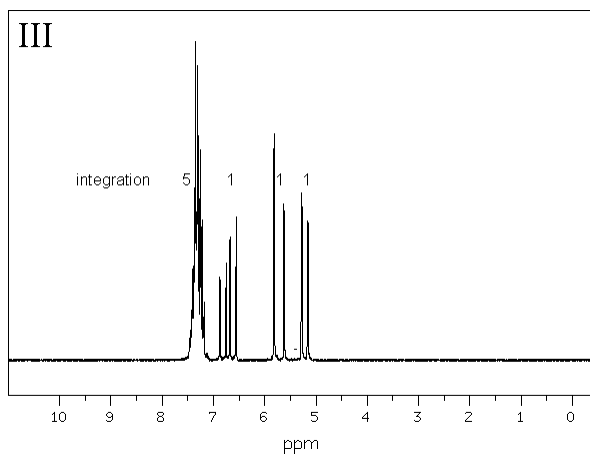
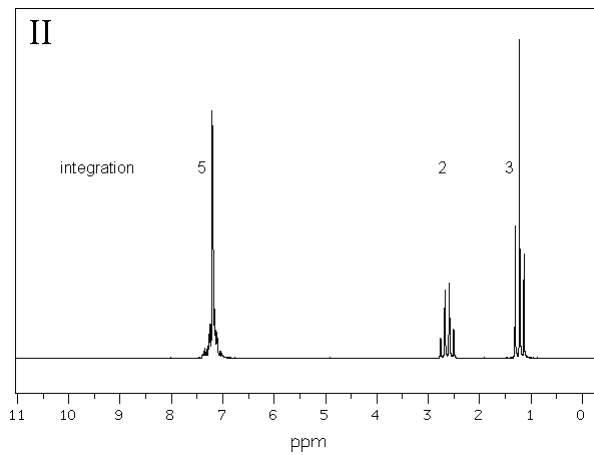
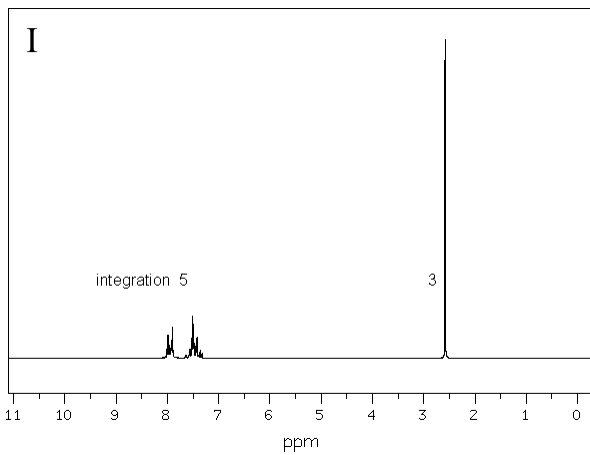
solvents
inorganic reagents
Any compounds with 3 or less C atoms

CONTINUED -->

PART 8: STRUCTURE DETERMINATION**12% WRITE YOUR ANSWER IN THE BOOKLET PROVIDED**

Based on the scheme of reactions shown below, identify the compounds **A - F** and match them to the appropriate H-nmr spectra **I-VI** provided on the following page.





*** THE END ***