THE UNIVERSITY OF CALGARY

FACULTY OF SCIENCE

MIDTERM EXAMINATION

CHEMISTRY 353

FEBRUARY 28th, 2001 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 - 39 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

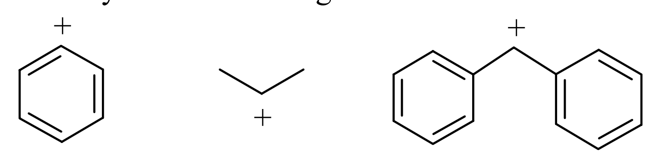
15% **ANSWER ANY FIVE (5) OF QUESTIONS 1-8**.

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.

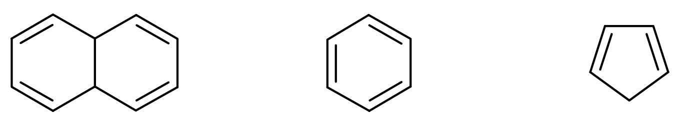
A.	**i > ii > iii**	**D**.	**ii > iii > i**
B.	**i > iii > ii**	**E**.	**iii > i > ii**
C.	**ii > i > iii**	**AB**.	**iii > ii > i**

1. The relative stability of the following carbocations:



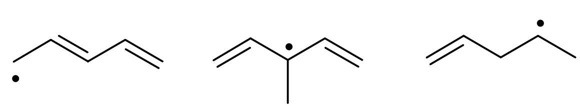
(i) (ii) (iii)

2. The resonance energies of each of the following:



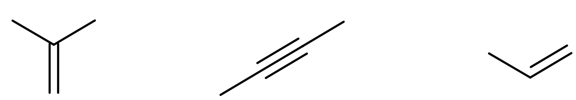
(i) (ii) (iii)

3. The relative stability of the following radicals:



(i) (ii) (iii)

4. The relative reactivity towards HCl of each of the following:

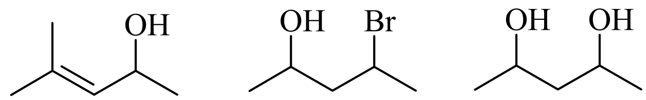


(i) (ii) (iii)

Use the following code to indicate your answers.

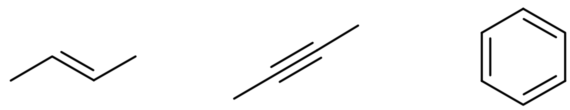
A.	**i > ii > iii**	**D.**	**ii > iii > i**
B.	**i > iii > ii**	**E.**	**iii > i > ii**
C.	**ii > i > iii**	**AB.**	**iii > ii > i**

5. The number of stereoisomers of each of the following:



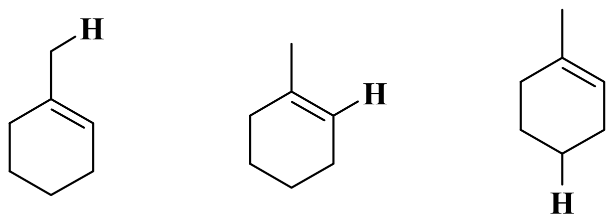
(i) (ii) (iii)

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



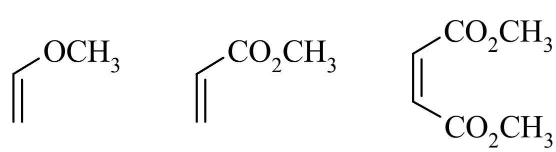
(i) (ii) (iii)

7. The homolytic bond energies of the following C-**H** bonds:



(i) (ii) (iii)

8. The relative reactivity towards 1,3-cyclopentadiene of the following:



(i) (ii) (iii)

PART 2: LABORATORY

9% **ANSWER ANY NINE (9) OF THE QUESTIONS 9-18.**

For each of the questions 9-18, decide whether the whole statement is true or false. If it is true then blacken **A**. If it is false then blacken **B**.

9. Lactose is a disaccharide of glucose and galactose.

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

11. The monomer units in PET plastic are terephthalic acid and ethylene glycol.

12. Kevlar and nylon are examples of polyamides.

13. A polyunsaturated fat will have a higher iodine number than a saturated fat.

14. Anhydrous magnesium sulphate can be used to remove traces of water from organic solutions.

15. Proline does not show as a blue spot when visualised with ninhydrin because it is a secondary amine.

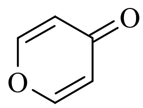
16. Addition of sulphuric acid to a soap causes precipitation because carboxylic acids are only weak acids and are less polar than the sodium carboxylate salts.

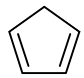
17. Chemically, saponification is the base promoted hydrolysis of amides.

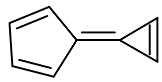
18. Hydrolysis of carboxylate esters gives carboxylic acids and alcohols.

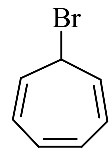
PART 3: AROMATICITY AND RESONANCE

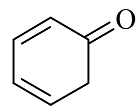
12% **ANSWER ANY SIX (6) of the questions 19-26.**

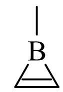

A

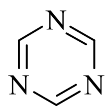

B

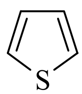

C

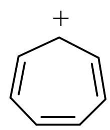

D

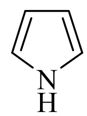

E

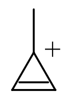

AB

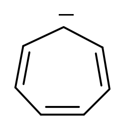

AC


AD


AE


BC


CD


CE

For each of the questions **19-26** select **a single compound** from the list above that is **best** described as:

19. Non-aromatic system as drawn with 4π-electrons.

20. An ionic, aromatic system where n=1 in the Huckel rule.

21. A system that readily undergoes a Diels-Alder reaction and has an aromatic conjugate base.

22. Aromatic as drawn and also has an aromatic conjugate acid

23. Aromatic as drawn but has a non-aromatic conjugate acid.

24. Non-aromatic as drawn but has an aromatic tautomer.

25. Non-aromatic as drawn, but has an important aromatic resonance structure.

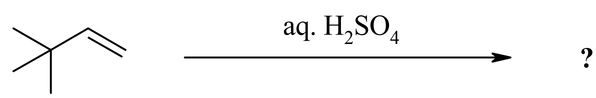
26. A system that is isoelectronic with benzene.

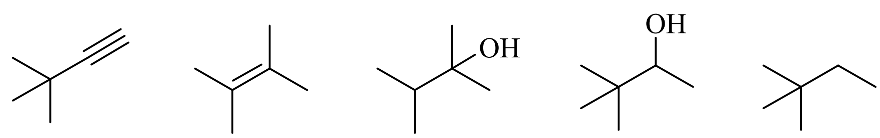
PART 4: STARTING MATERIALS AND PRODUCTS OF REACTIONS

15% **ANSWER ANY SIX (6) OF QUESTIONS 27-33.**

For each of questions **27-33** select either the major product or the starting material required in order to complete of the reaction schemes.

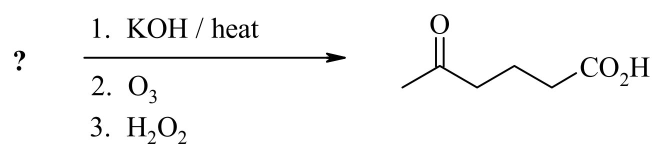
27.

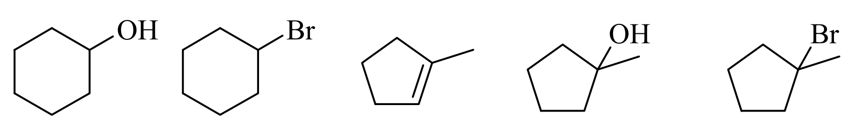




A **B** **C** **D** **E**

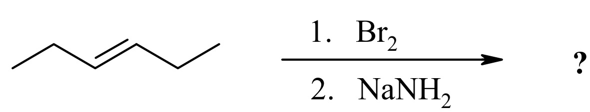
28.

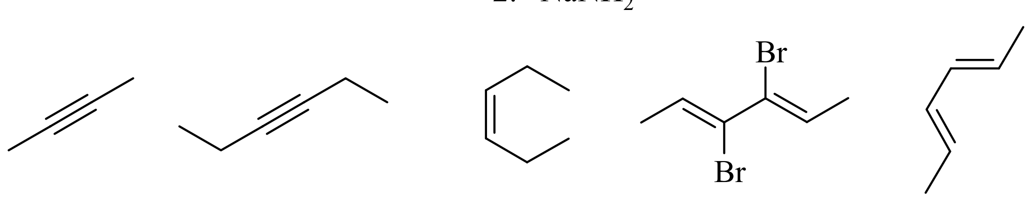




A **B** **C** **D** **E**

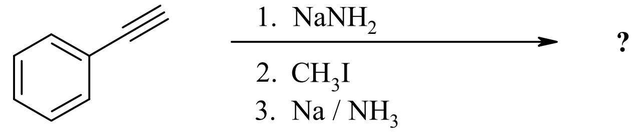
29.

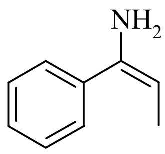




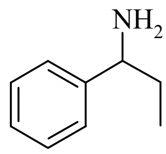
A **B** **C** **D** **E**

30.

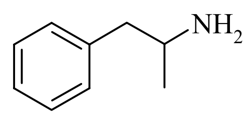




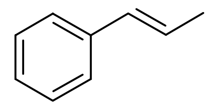
A



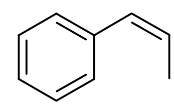
B



C

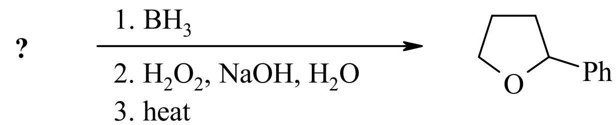


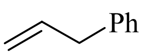
D



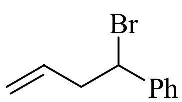
E

31.

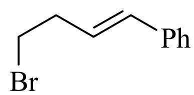




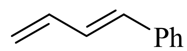
A



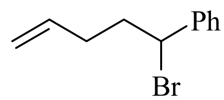
B



C

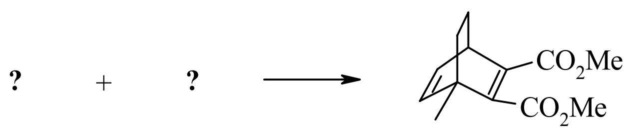


D

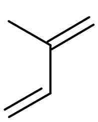


E

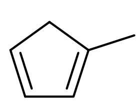
The last two questions **both apply** to the following reaction scheme:



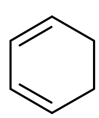
32.



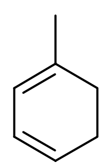
A.



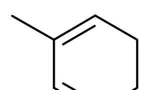
B.



C.

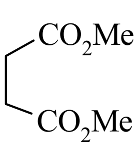


D.

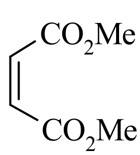


E.

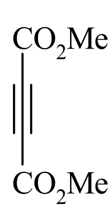
33.



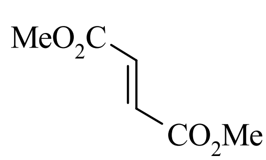
A.



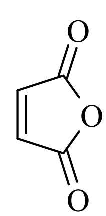
B.



C.



D.



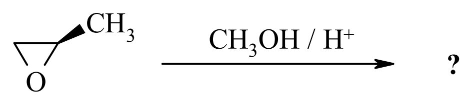
E.

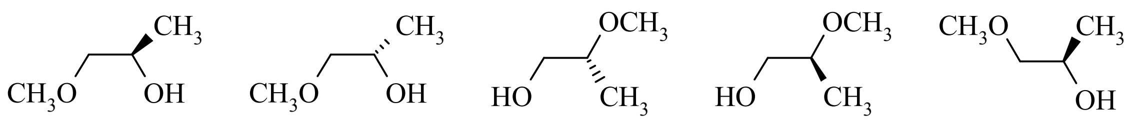
PART 5: REGIO- and STEREOCHEMISTRY OF REACTIONS

15% **ANSWER ANY FIVE (5) OF QUESTIONS 34-39**.

For each of the questions **34 - 39**, select the most abundant product. If two products are equally abundant, then indicate both. In order to indicate more than one product, blacken the spaces corresponding to each one.

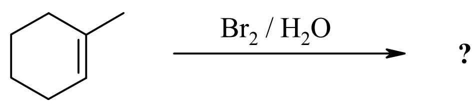
34.

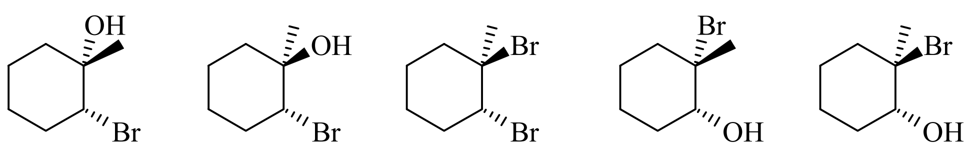




A **B** **C** **D** **E**

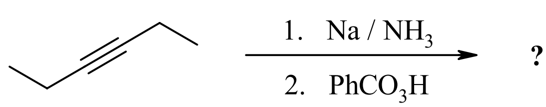
35.

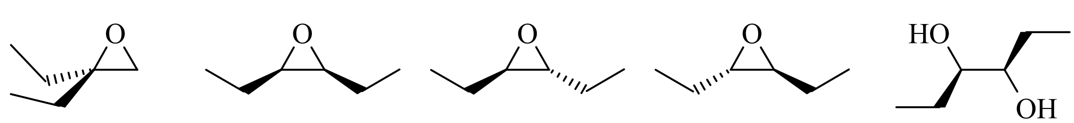




A **B** **C** **D** **E**

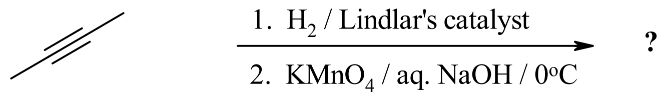
36.

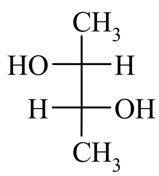




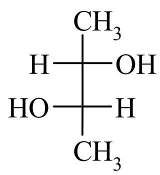
A **B** **C** **D** **E**

37.

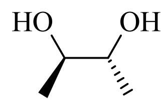




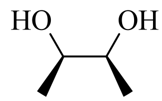
A



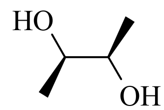
B



C

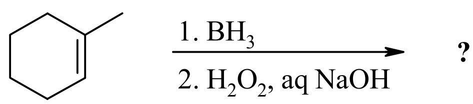


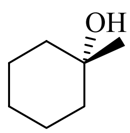
D



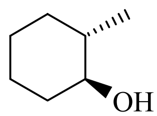
E

38.





A



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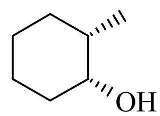

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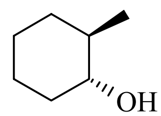

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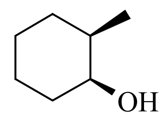
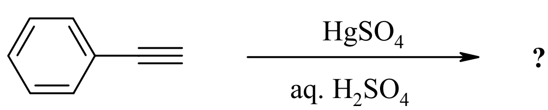
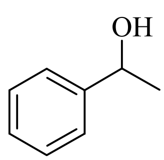


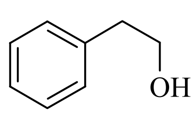
E

39.





A



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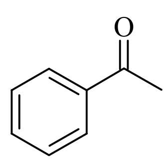

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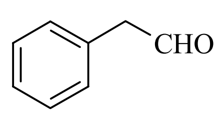

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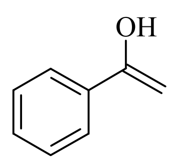


E

PART 6: MECHANISMS

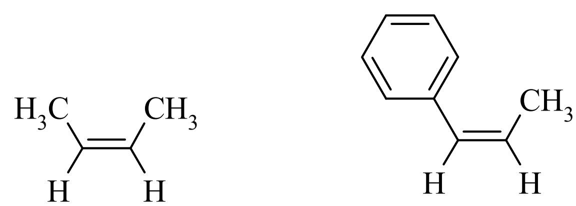
10% **ANSWER ANY TWO (2) OF QUESTIONS A - C**

WRITE YOUR ANSWER IN THE BOOKLET PROVIDED

Use curly arrow mechanisms to answer each of the following questions

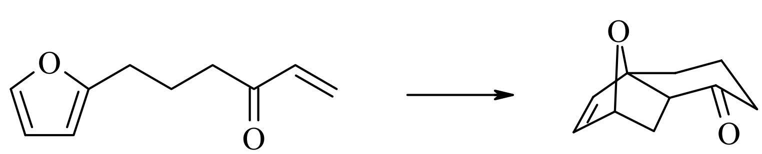
A. Use your knowledge of the reactions of alkenes with halogens and hypohalous acids to predict the outcome of the following reaction :

B Explain the following data for the addition of Br_2 to two different *cis*-alkenes in acetic acid at 25 °C



100 % anti addition 73 % anti addition

C Suggest a mechanism for the following transformation (no other reagents are required):



PART 7 : STRUCTURE DETERMINATION

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

Compound **A** is a hydrocarbon with analysis 88.16 %C, 11.84 %H by weight. When **A** was subjected to ozonolysis followed by work-up with Zn / CH_3CO_2H it gave a single compound **B**, C_5H_8O. **B** did not react with hydrogen / palladium, and gave an orange precipitate when tested with 2,4-DNP.

In a separate series of reactions, **A** was treated first with Br_2/CH_2Cl_2 giving a colourless solution from which **C** $C_{10}H_{16}Br_2$ was obtained. When **C** was heated with KOH / EtOH it gave the hydrocarbon **D** $C_{10}H_{14}$ that decolourised Br_2/CH_2Cl_2. On reaction of **A** with $KMnO_4$ / NaOH / 0^oC the purple solution went colourless and gave **E** $C_{10}H_{18}O_2$ which when heated with H_2SO_4 also gave **D**.

When catalytically hydrogenated, both **A** and **D** gave dicyclopentane.

When **D** was reacted with ethene and heated, it gave **F** $C_{12}H_{18}$, a meso compound, that decolourised Br_2/CH_2Cl_2. On ozonlysis with work-up using hydrogen peroxide, **D** also gave a single compound: 5,6-dioxodecanedioic acid.

None of the compounds **A** – **F** are chiral.

The broadband decoupled ^{13}C-nmr of each of the compounds showed the following number of peaks:

A = 3, **B** = 3, **C** = 3, **D** = 5, **E** = 3, **F** = 6

Identify **A** - **F**.

Why is **F** a meso compound ? Show it's chiral centers and assign their configurations.

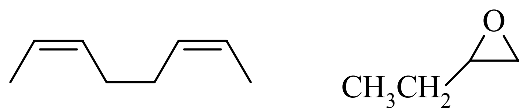
PART 8: SYNTHESIS

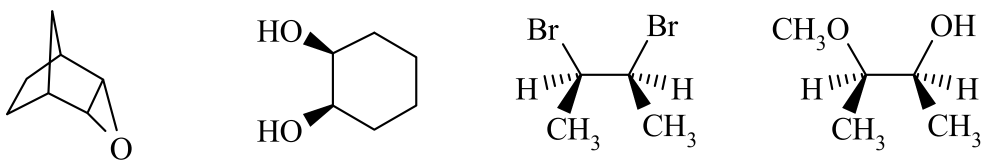
12% Using any of the starting materials shown, design efficient syntheses of any **THREE (3)** of the following molecules.

WRITE YOUR ANSWERS IN THE BOOKLET PROVIDED.

DO NOT SHOW MECHANISMS.

$CH_3-C\equiv C-CH_2CH_2OH$





Allowed Starting Materials:

solvents
inorganic reagents
Any compounds with 3 or less C atoms