THE UNIVERSITY OF CALGARY

FACULTY OF SCIENCE

MIDTERM EXAMINATION

CHEMISTRY 353

MARCH 2nd, 2004 Time: 2 Hours

PLEASE WRITE YOUR NAME AND FULL STUDENT I.D. NUMBER ON BOTH YOUR COMPUTER ANSWER SHEET and on 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 included with this examination paper.

Parts 1 - 5 consist of a series of multiple choice questions numbered 1 - 45 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 soft 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

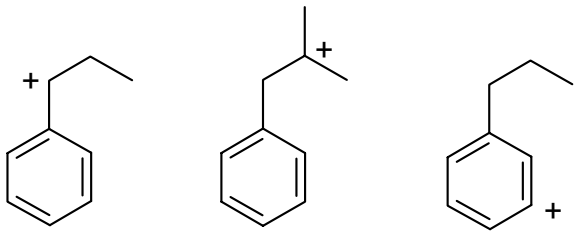
12% **ANSWER ANY SIX (6) OF QUESTIONS 1-8**.

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.

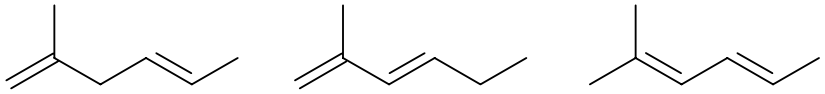
A.	**i > ii > iii**	**D**.	**ii > iii > i**
B.	**i > iii > ii**	**E**.	**iii > i > ii**
C.	**ii > i > iii**	**AB**.	**iii > ii > i**

1. The relative stability of the following carbocations :



i **ii** **iii**

2. The relative heat of hydrogenation of the following (most endothermic to most exothermic) :



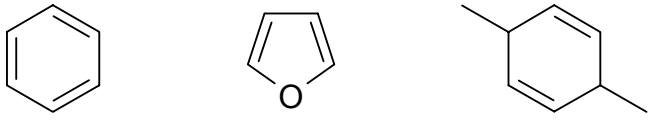
i **ii** **iii**

3. The relative acidity of the **H** atom in each of the following:

HO–**H** $CH_3C{\equiv}C$–**H** $(CH_3)_3CO$–**H**

i **ii** **iii**

4. The relative resonance energies of each of the following:



i **ii** **iii**

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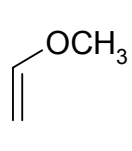
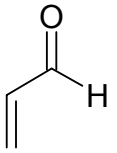
Use the following code to indicate your answers.

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 relative reactivity towards 1,3-cyclopentadiene of each of the following:



i



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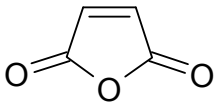
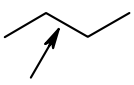
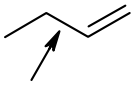


iii

6. The bond length of the following C to C bonds (C2-C3):



i



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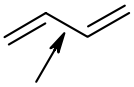
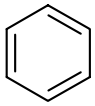
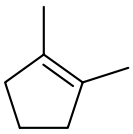


iii

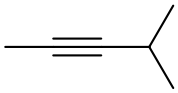
7. The relative reactivity of each of the following towards H_2 / Pd :



i

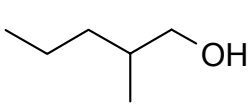


ii

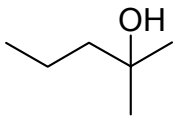


iii

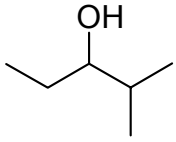
8. The relative yields of the following products from the reaction of 2-methyl-1-pentene with BH_3 followed by the normal work-up with aq. NaOH / H_2O_2 :



i



ii



iii

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PART 2: LABORATORY

14% **ANSWER ANY FOURTEEN (14) OF THE SIXTEEN (16) TRUE / FALSE QUESTIONS 9-24.**

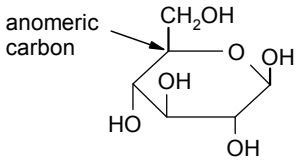
Questions 9-24 are based on the laboratory component of Chem 353. In each case decide whether the statements are true or false. If the statement is true select "**A**", if it is "false" then select "**B**"

Questions 9-12 are from the experiment about the hydrolysis of sucrose.

9. Glucose is an example of a monosaccharide.

10. The reaction is acid catalysed because the sucrose needs to be protonated in order for the glycosidic bond to break.

11. The carbon atom indicated in the following diagram is an example of an anomeric carbon atom.



12. Rate of reaction = k_1 [A][B] and rate of reaction = k_2 $[A]^2$ are both examples of reactions that are second order.

Questions 13-16 are from the experiment about the chemistry of alcohols.

13. Alcohol reactivity towards acid catalysed dehydration follows a reactivity order that reflects the stability of the carbocation intermediate that is formed in an E1 type of elimination.

14. The Lucas test where $ZnCl_2$ and HCl are reacted with an alcohol generally follows the reactivity order where $1^o > 2^o > 3^o$.

15. Secondary alcohols are typically oxidised by chromium reagents to aldehydes or carboxylic acids.

16. 2,4-dinitrophenylhydrazine reacts with the carbonyl group in aldehydes, ketones, carboxylic acids and esters to give a yellow to red precipitate.

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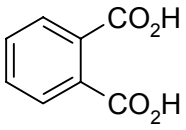
Questions 17-20 are from the experiment about polymers and plastics.

17. Kevlar and nylon are both examples of polyamides.

18. Terephthalic acid is a dicarboxylic acid with the structure shown



19. Esters can be hydrolysed with either aqueous acid or aqueous base reaction conditions.

20. The ester functional group is typically represented as RCO_2R'

Questions 21-24 are from the experiment about the synthesis of benzoic acid.

21. Grignard reagents are a source of electrophilic carbon atoms.

22. The final organic product was obtained as an insoluble precipitate by acidifying the aqueous mixture because the product is formed as a soluble, weakly basic carboxylate salt.

23. The reaction using the Grignard reagent was done using dry glassware and solvents because benzoic acid reacts with water.

24. Grignard reagents are examples of organometallic compounds where the metal involved is sodium.

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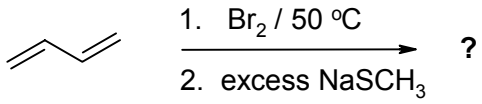
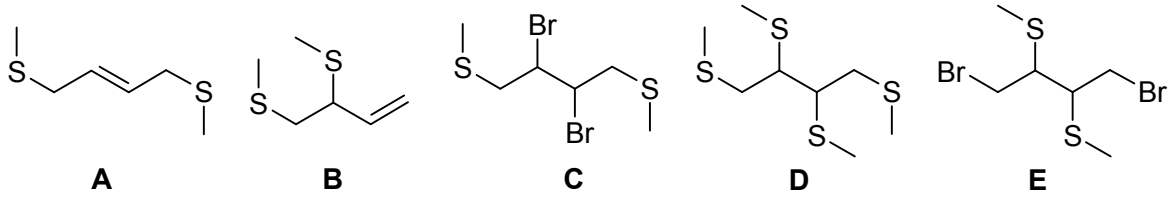
PART 3: STARTING MATERIALS AND PRODUCTS OF REACTIONS

12% **ANSWER ANY SIX (6) OF QUESTIONS 25-31.**

For each of questions **25-31** select either the major product or the starting material required in order to complete of the reaction schemes.

25.





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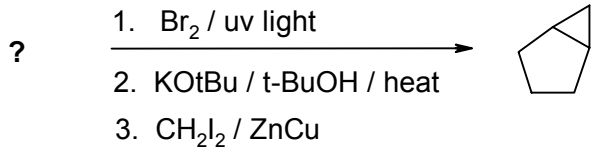

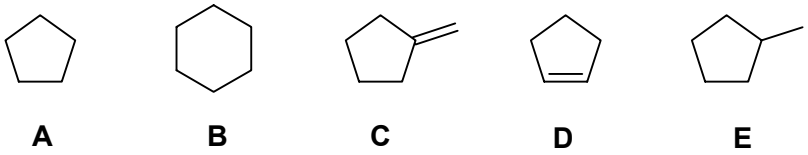

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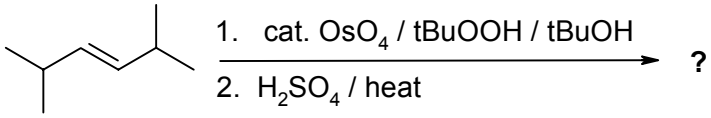

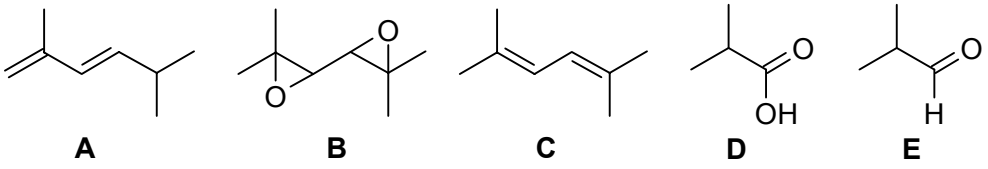

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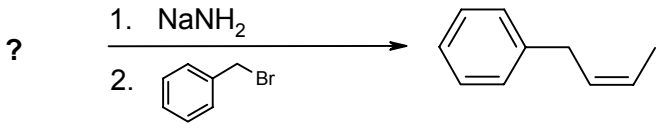
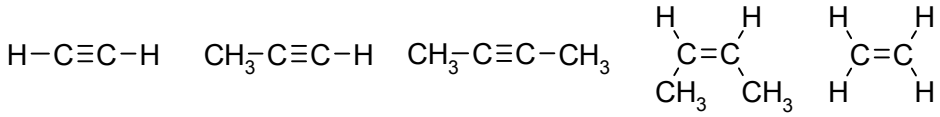
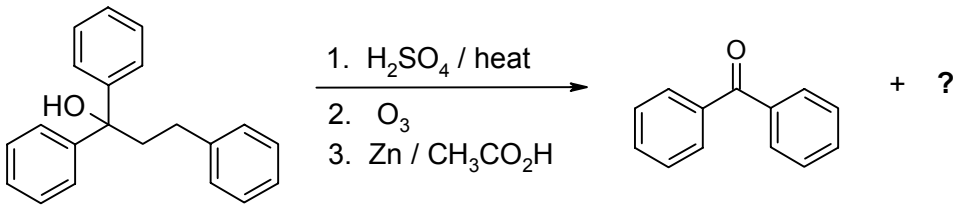
28.

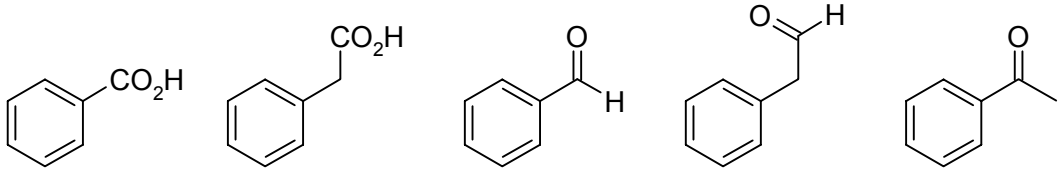




A **B** **C** **D** **E**

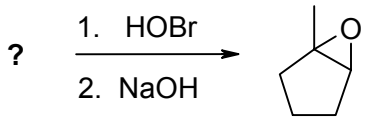
29.

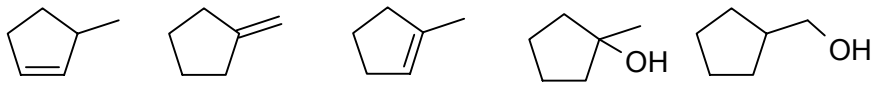




A **B** **C** **D** **E**

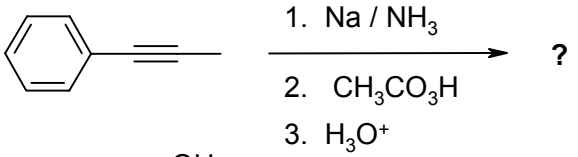
30.

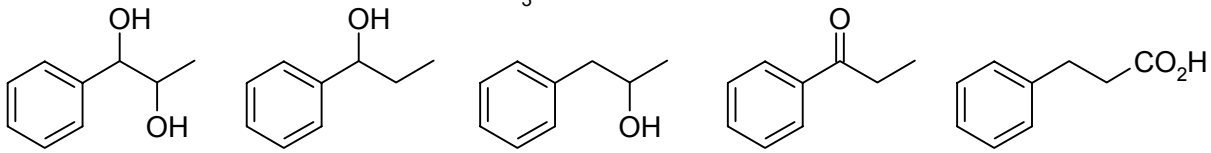




A **B** **C** **D** **E**

31.





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

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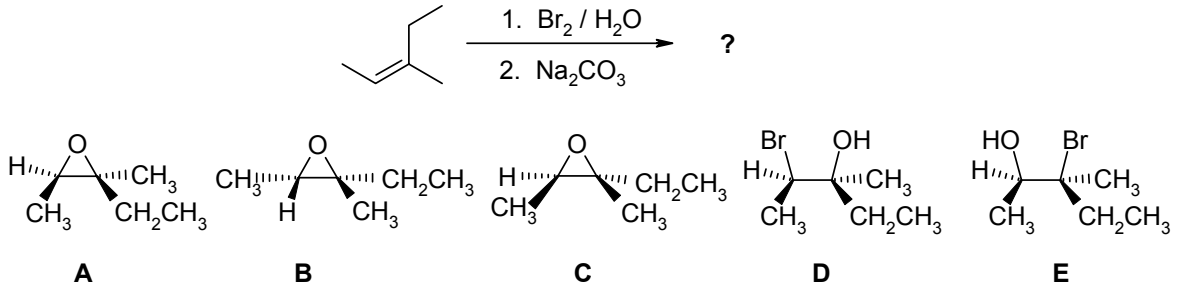
PART 4: REGIOCHEMISTRY and STEREOCHEMISTRY OF REACTIONS

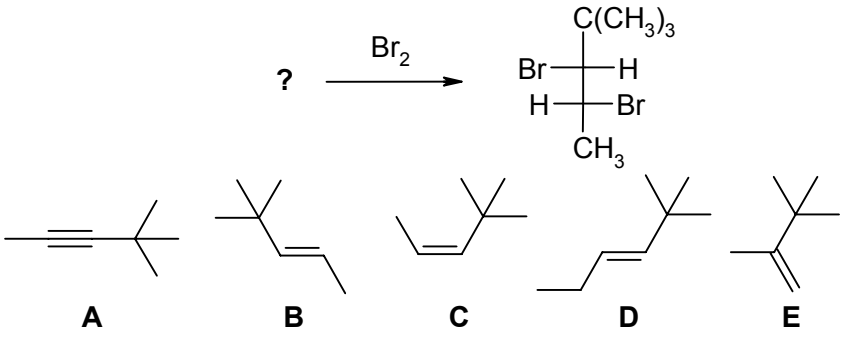
15% **ANSWER ANY FIVE (5) OF QUESTIONS 32-37**.

For each of the **questions 32-37**, 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.

32.



33.



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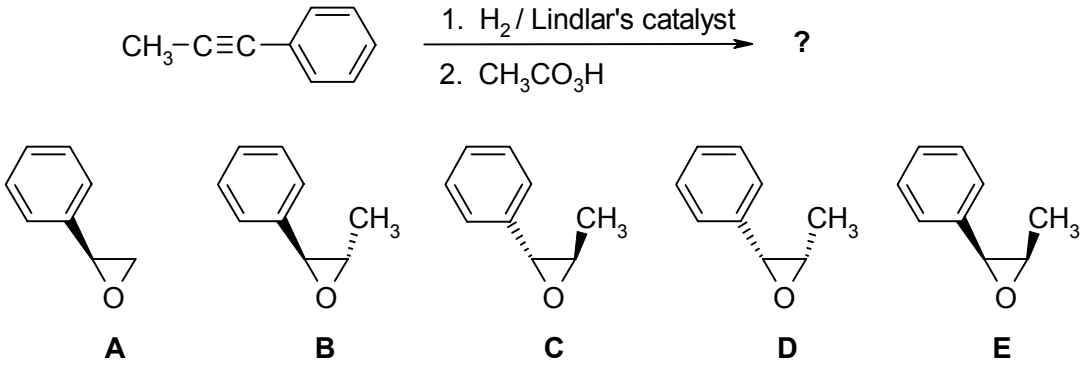

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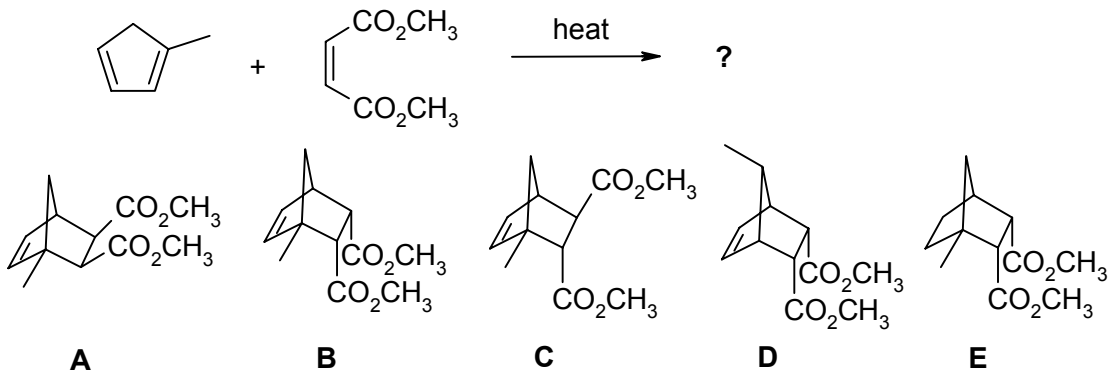
35.



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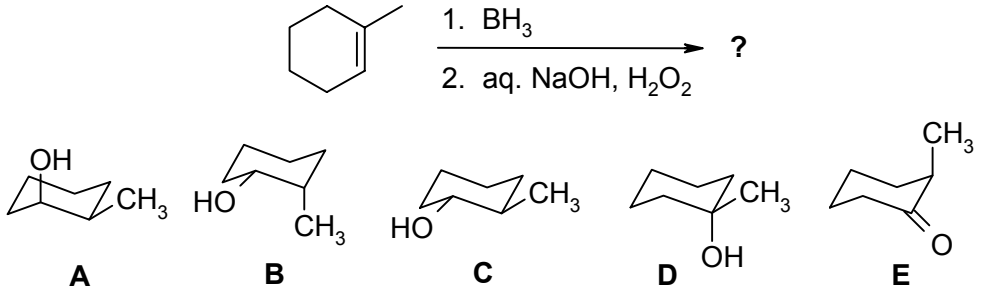

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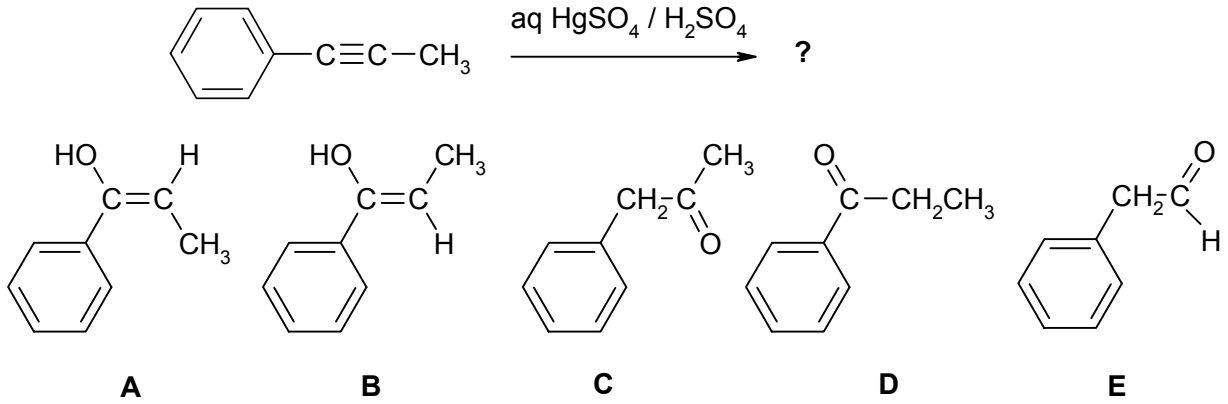

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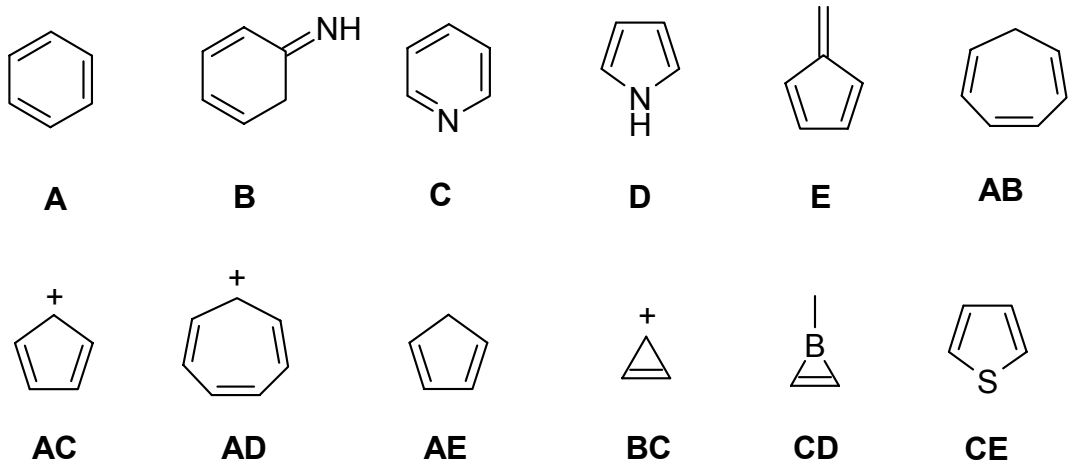
PART 5: AROMATICITY AND RESONANCE

12% **ANSWER ANY SIX (6) of the questions 38 - 45.**



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

AC **AD** **AE** **BC** **CD** **CE**

For each of the **questions 38-45** select **a single compound** from the list above that is **best** described as:

38. Non-aromatic as drawn with 4 π-electrons.

39. Aromatic as drawn and also has a non-aromatic conjugate acid.

40. Non-aromatic as drawn and also has an aromatic conjugate base.

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

42. A heteroaromatic system that is isoelectronic with benzene.

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

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

45. An anti-aromatic system.

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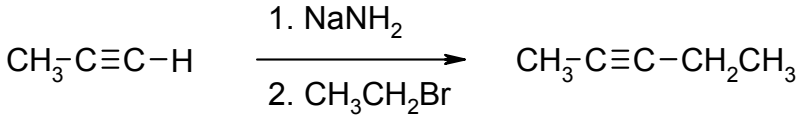
PART 6: MECHANISMS

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

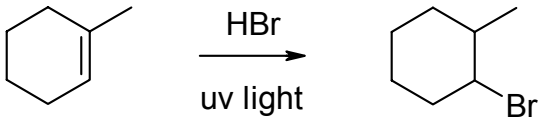
WRITE YOUR ANSWER IN THE BOOKLET PROVIDED

Draw curly arrow mechanisms to explain any two (2) of the following reactions / observations. No other reagents are required.

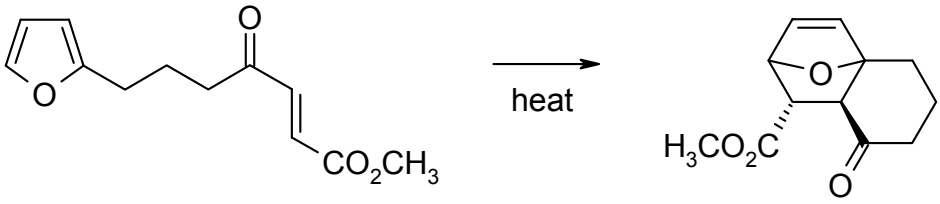
A. Show the mechanism for the following reaction sequence:



B Show the mechanism for the following reaction and rationalise the regiochemistry :



C Show the mechanism for the following reaction :



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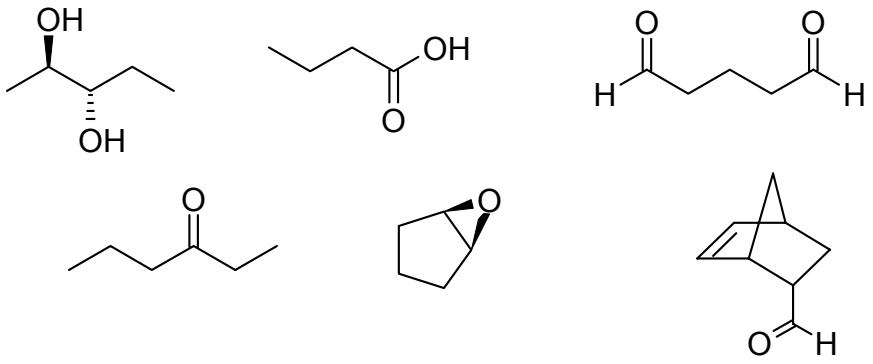
PART 7: SYNTHESIS

12% **WRITE YOUR ANSWERS IN THE BOOKLET PROVIDED**.

DO NOT SHOW MECHANISMS.

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



Allowed starting materials and reagents

solvents
inorganic reagents
any **hydrocarbons** with 3 or less C atoms

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PART 8: STRUCTURE DETERMINATION

13% **WRITE YOUR ANSWER IN THE BOOKLET PROVIDED**

Use the information in the following paragraph to answer the questions below.

A, $C_5H_{12}O$, IR : 3500cm^{-1} (very broad), reacted only very slowly with the Lucas reagent ($ZnCl_2$ / HCl) giving a small amount of a second colourless layer. When **A** was converted to the tosylate using tosyl chloride (TsCl) and Et_3N, and then heated with KOH, **B**, C_5H_{10} was obtained, IR :1680 cm^{-1} (w). **B** gave a colourless solution when tested with Br_2 in chloroform. Subsequent reaction of **B** with Br_2 under a uv lamp or with N-bromosuccinimide gave **C**, C_5H_9Br as the major product. Reaction of **B** with BH_3 then aq. NaOH / H_2O_2 gave **A** as the major product. In contrast, reaction of **B** with aq. H_2SO_4 gave **D** as the major product. **D**, IR : 3500cm^{-1} (very broad), reacted rapidly with the Lucas reagent and was found to be an isomer of **A**.

When **C** was reacted with hot, ethanolic KOH, **E**, C_5H_8 was formed. **E** was found to have 5 peaks in the ^{13}C-nmr. When **E** was heated in a sealed tube with ethene, it gave **F**, C_7H_{12}, as the major product. **F**, IR : 1660cm^{-1}, 7 peaks in the ^{13}C-nmr also gave a colourless solution with Br_2 in chloroform. Subsequent reaction of **F** with ozone followed by hydrogen peroxide work up gave 6-oxo-heptanoic acid.
None of the materials **A - F** are chiral.

- Identify the compounds **A - F** (structures are sufficient) (9 marks)

- Draw a curly arrow mechanism to show ***EITHER*** the reaction of **B** to give **D** ***OR*** the reaction of **E** with ethene to give **F**. (2 marks)

- Which compound of **A-F** has the following ^{1}H-nmr spectra data : 1.52 ppm (broad, singlet, 1H), 1.49 ppm (quartet, 2H), 1.20 ppm (singlet, 6H) and 0.92 ppm (triplet, 3H). (2 marks)

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

HH / IRH / W04