THE UNIVERSITY OF CALGARY

FACULTY OF SCIENCE

MIDTERM EXAMINATION

CHEMISTRY 353

MARCH 9th, 2005 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.

Absolutely no electronic devices are allowed.

PART 1: RELATIVE PROPERTIES

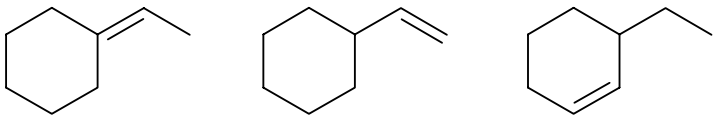
12% **ANSWER ANY SIX (6) OF QUESTIONS 1-8**.

Arrange the items in each of 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.

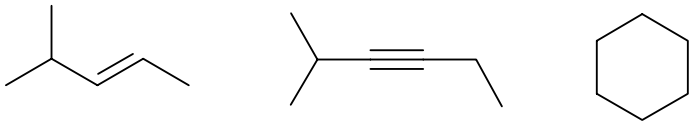
A.	**i > ii > iii**	**D**.	**ii > iii > i**
B.	**i > iii > ii**	**E**.	**iii > i > ii**
C.	**ii > i > iii**	**AB**.	**iii > ii > i**

1. The relative number of the allylic hydrogens in each of the following:



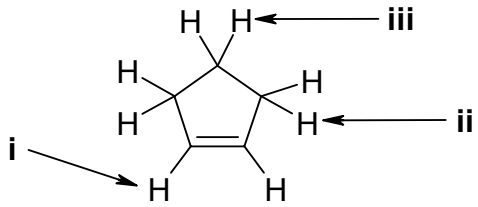
i **ii** **iii**

2. The relative reactivity towards aq. sulfuric acid of each of the following:

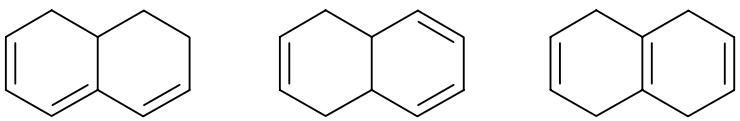


i **ii** **iii**

3. The relative acidity of the hydrogen atoms indicated:



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



i **ii** **iii**

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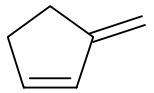
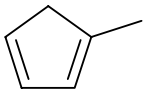
Use the following code to indicate your answers.

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

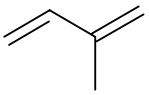
5. The relative reactivity towards methyl propenoate of each of the following:



i

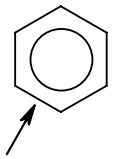


ii

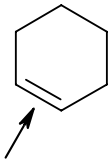


iii

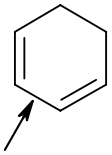
6. The bond length of the following C to C bonds:



i

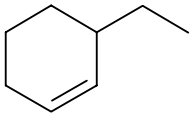


ii

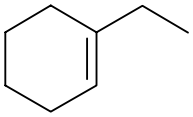


iii

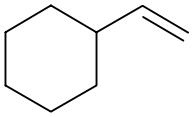
7. The relative reactivity of each of the following towards CH_3CO_3H:



i

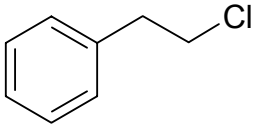


ii

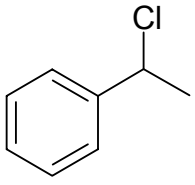


iii

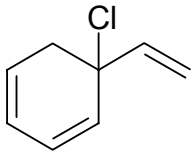
8. The relative yields of the following products from the reaction of phenylethene (also known as styrene) with HCl:



i



ii



iii

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PART 2: LABORATORY

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

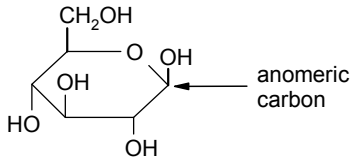
Questions 9-24 are based on the laboratory component of Chem 353. In each case decide whether the statements are true or false. If the statement is true select "A", if it is "false" then select "B"

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

9. Sucrose is an example of a monosaccharide.

10. Specific rotation, $[\alpha] = \alpha / c\ L$ where α = observed rotation, c = concentration in g/mL and L = path length measured in dm.

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



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

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

13. Dehydration of alcohols in concentrated acid follows a reactivity trend characteristic of a mechanism involving carbocations.

14. The insoluble product formed in the Lucas test (reagents = $ZnCl_2$ / HCl) is an alkyl chloride.

15. Tertiary alcohols are not oxidised by chromium reagents.

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

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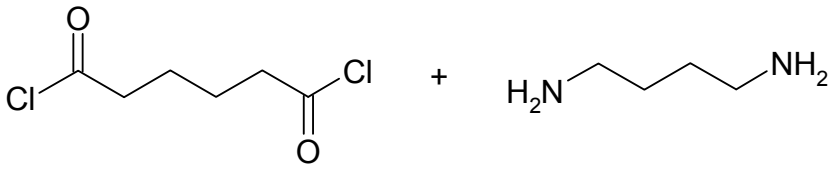
Questions 17-20 are from the experiment about polymers and plastics.

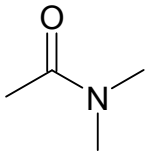
17. Nylon [6.6] is can be made using the reaction of the following reagents:



18. When a "condensation polymer" is formed, a small molecule such as water is also formed, hence the term "condensation".

19. In a reflux apparatus, the vertical condenser is normally cooled with a steady flow of cold water.

20. The following structure shows an amide functional group:



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

21. Grignard reagents are examples of organomagnesium compounds.

22. The role of the iodine was to react with the bromobenzene to make iodobenzene in order to make the aryl halide system more reactive.

23. The "work-up" step involved adding water and acid in order to neutralise the strongly basic conditions.

24. A cryogen is a material that can causes burns to the skin due to being very cold.

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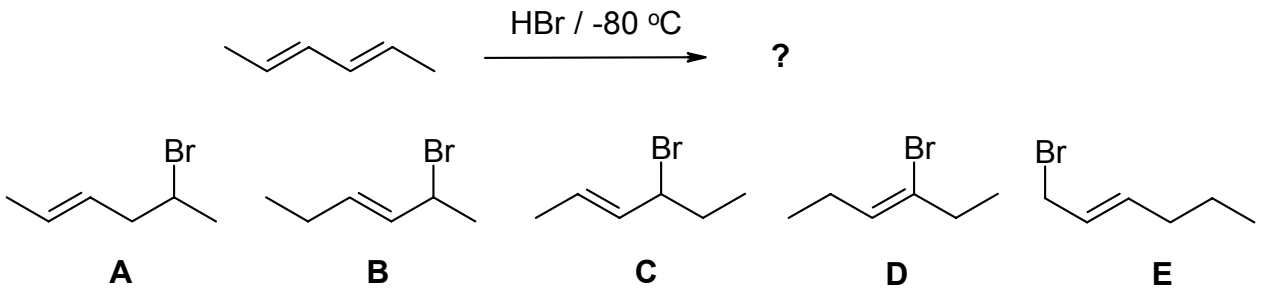
PART 3: STARTING MATERIALS, REAGENTS AND PRODUCTS

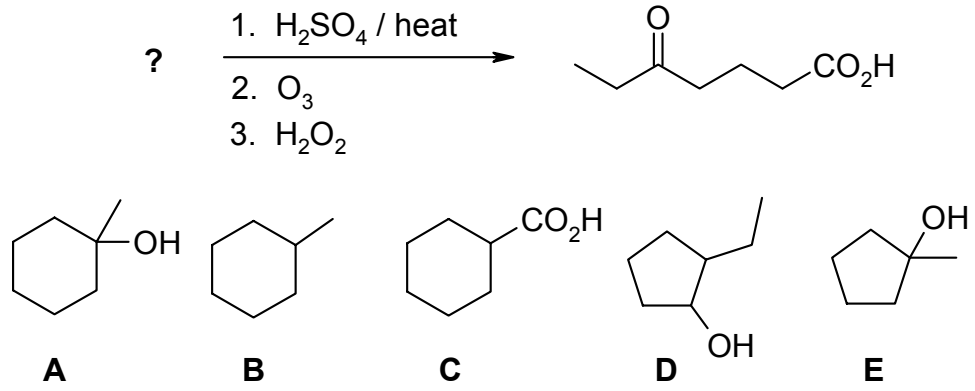
12% **ANSWER ANY SIX (6) OF QUESTIONS 25-31.**

For each of questions 25-31 select the MISSING component (the starting material, the product or the reagents) required in order to BEST complete each of the reaction schemes.

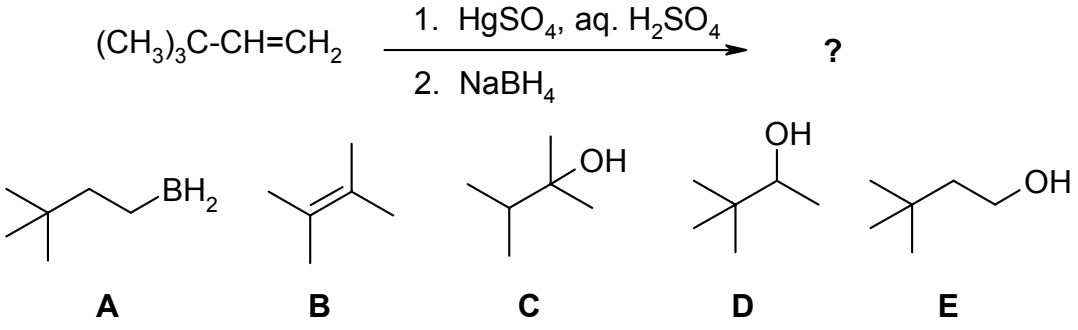
25.



26.



27.



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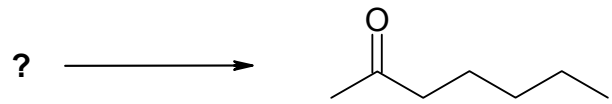
28.



A 1. ethyne, $NaNH_2$ 2. 1-bromopentane 3. H_3O+, $HgSO_4$

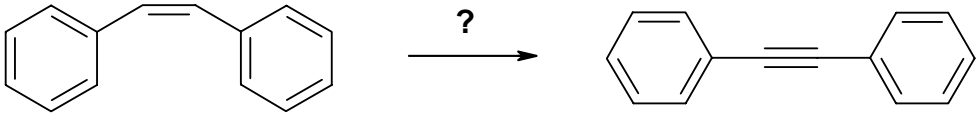
B 1. propyne, $NaNH_2$ 2. 1-bromobutane 3. H_3O+, $HgSO_4$

C 1. 1-butyne, $NaNH_2$ 2. 1-bromopropane 3. H_3O+, $HgSO_4$

D 1. 1-pentyne, $NaNH_2$ 2. bromoethane 3. H_3O+, $HgSO_4$

E 1. 1-hexyne, $NaNH_2$ 2. bromomethane 3. H_3O+, $HgSO_4$

29.



A 1. HBr 2. excess $NaNH_2$

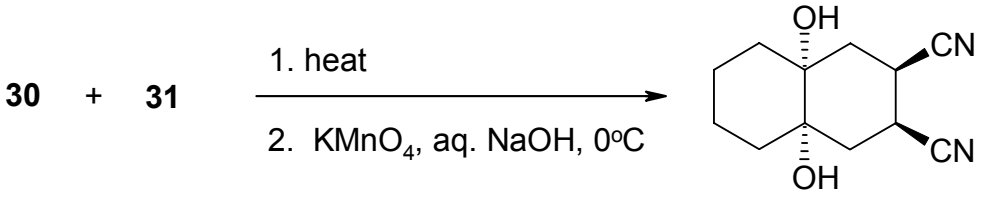
B 1. Br_2 2. excess $NaNH_2$

C H_2 / Lindlar's catalyst

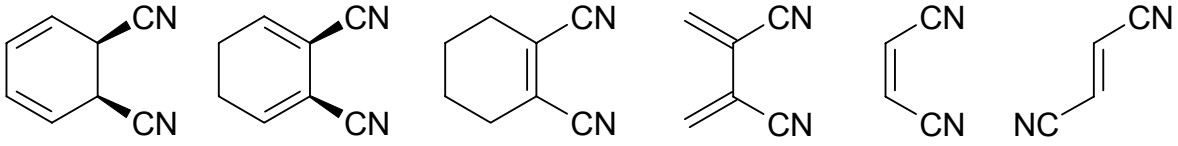
D 1. aq. H_2SO_4 2. H_2SO_4 / heat

E H_2SO_4 / heat

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

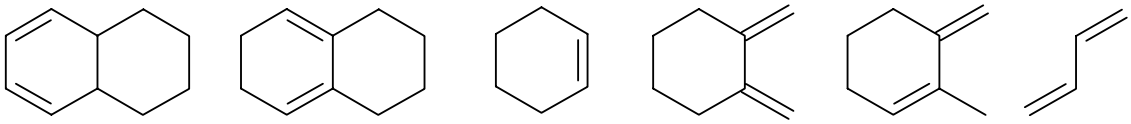


30.



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

31.



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

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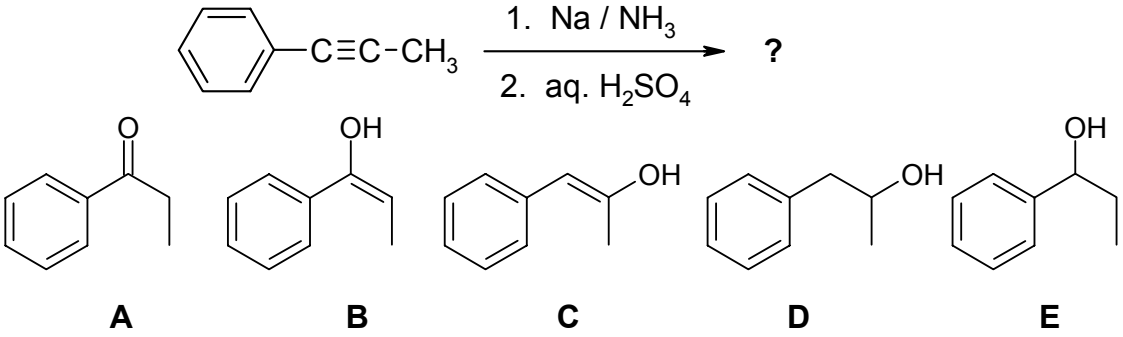
PART 4: REGIOCHEMISTRY and STEREOCHEMISTRY OF REACTIONS

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

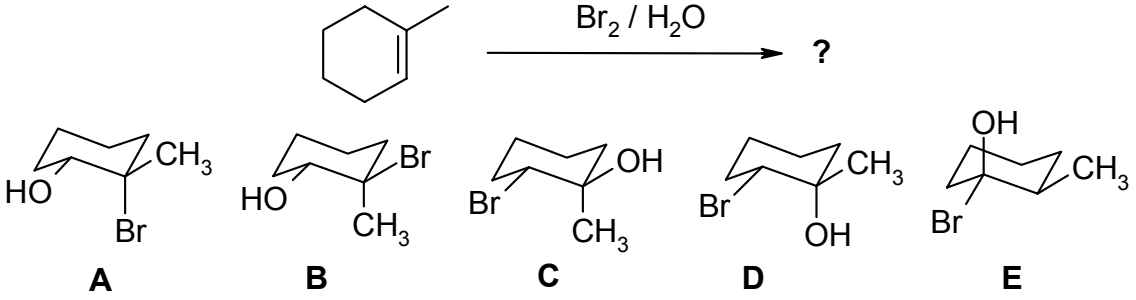
For each of the questions 32-37, select the structure required to complete the reaction shown. If two products are equally abundant, then you must indicate both for full marks. If two starting materials will give the same product, then you must indicate both for full marks. In order to indicate more than one structure, blacken the spaces corresponding to each one.

32.



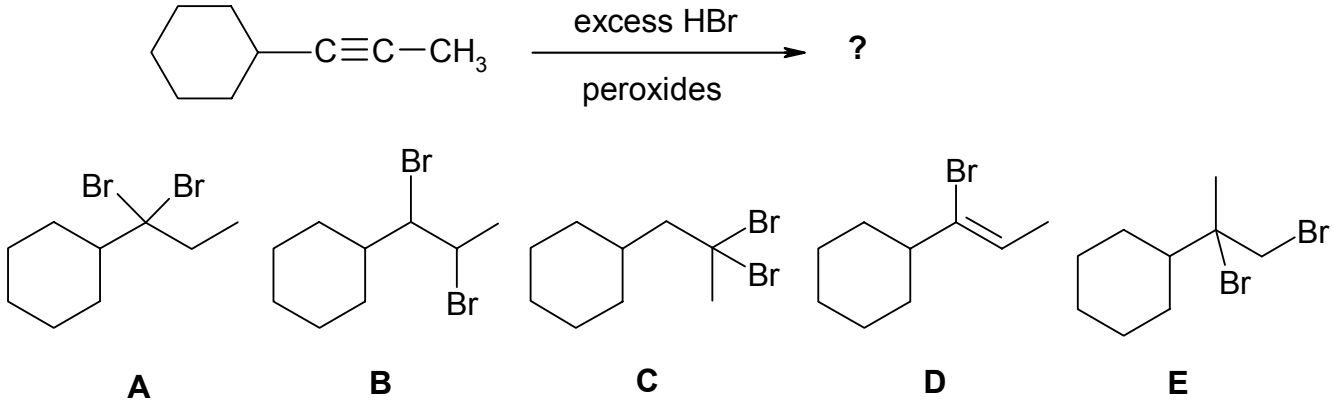
A **B** **C** **D** **E**

33.



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

34.



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

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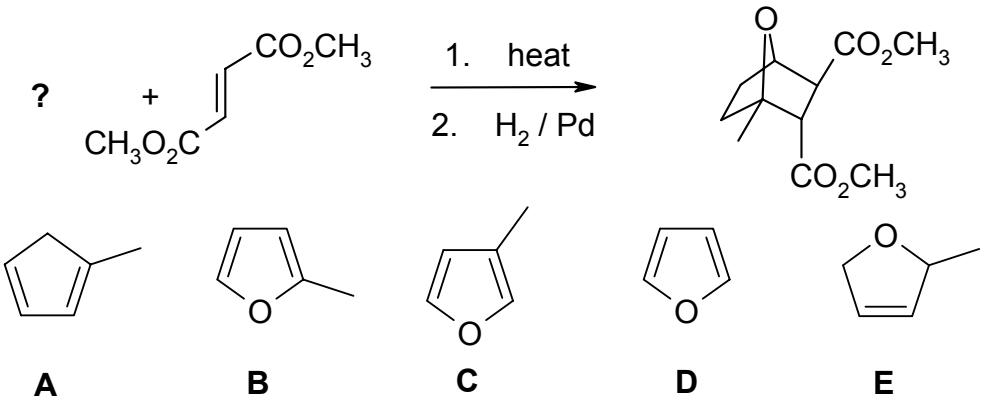
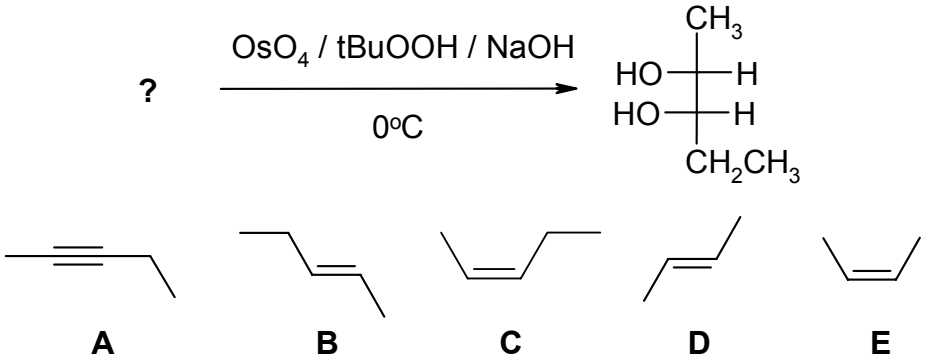
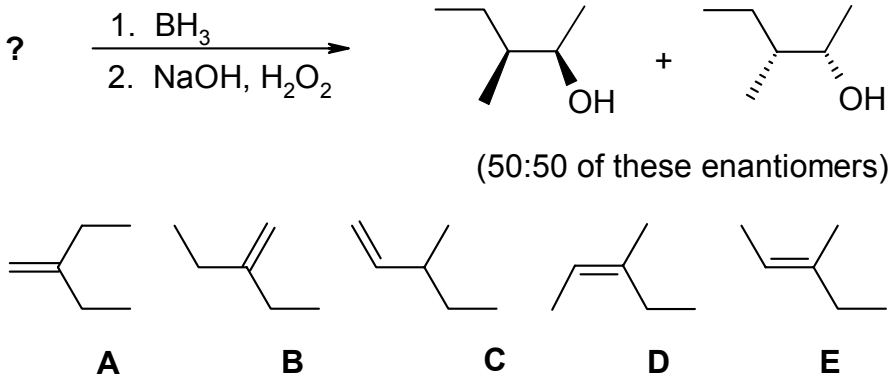
35.



36.



37.



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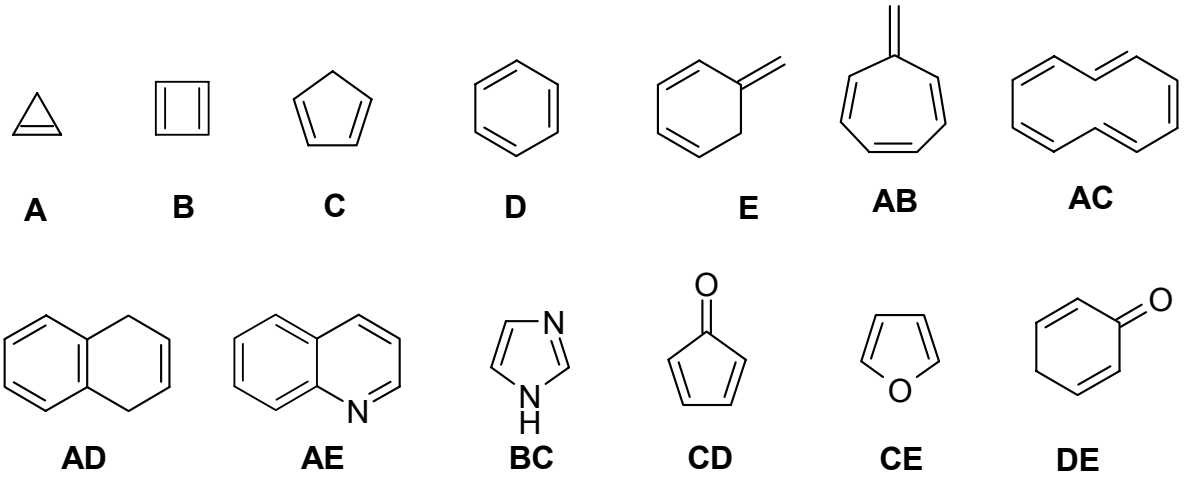
PART 5: AROMATICITY AND RESONANCE

14% **ANSWER ANY SEVEN (7) of the questions 38 - 45.**



For each of the questions 38-45 select <u>a single compound</u> from the list above that <u>best</u> matches each of the following descriptions:

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

39. A non-conjugated molecule.

40. A non-aromatic, conjugated triene.

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

42. An aromatic system where n=2 in the Huckel rule.

43. The most acidic hydrocarbon (since the resultant conjugate base is aromatic).

44. An aromatic system where n=1 in the Huckel rule that also has an aromatic conjugate acid.

45. Non-aromatic as drawn, but would react rapidly with an acid to give an aromatic carbocation.

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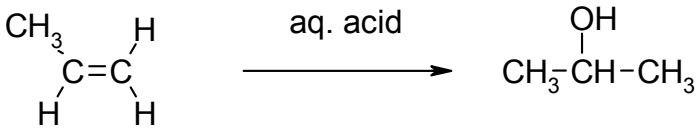
PART 6: MECHANISMS

8% **ANSWER ANY TWO (2) OF QUESTIONS A - C**

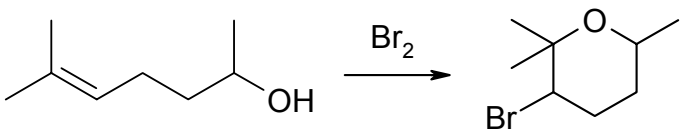
WRITE YOUR ANSWER IN THE BOOKLET PROVIDED

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

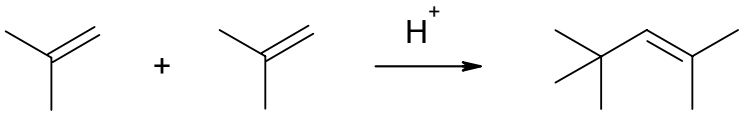
A. Show the mechanism for the following reaction sequence:



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



C Show the mechanism for the following reaction:



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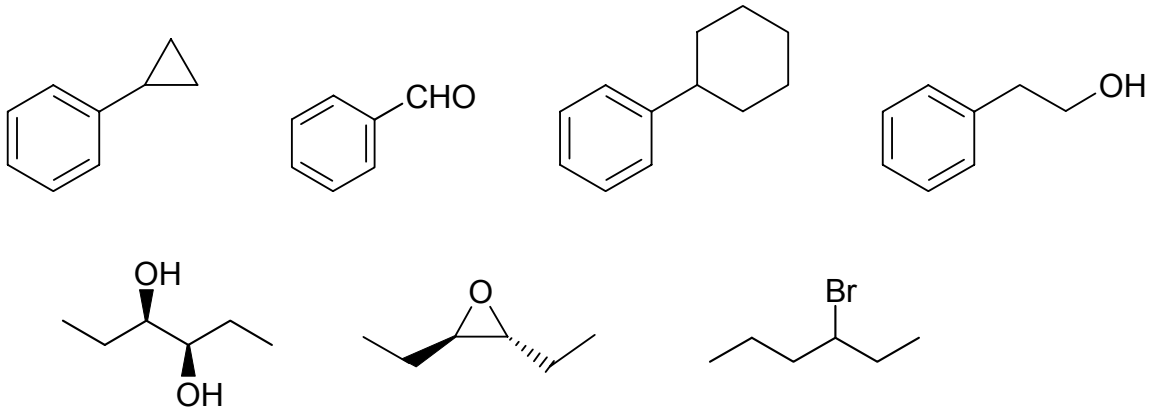
PART 7: SYNTHESIS

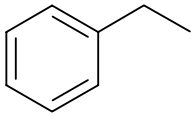
12% **WRITE YOUR ANSWERS IN THE BOOKLET PROVIDED**.

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



inorganic reagents

any **hydrocarbons** with 4 or less C atoms

You may use any solvents you wish (but they can not become part of the structure, *i.e.* they can be used as solvents not as starting materials or reagents)

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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 sample of **A**, C_5H_8, IR: 2120 cm^{-1}, was reacted with sodium amide then treated with n-propyl bromide to give **B**, C_8H_{14}. **B** was then reacted with hydrogen / Lindlar's catalyst to give **C**, C_8H_{16} that gave a colourless solution when tested with Br_2 in chloroform. Reaction of **C** with aq. alkaline $KMnO_4$, gave **D**, $C_8H_{18}O_2$ as a pair of enantiomers, IR: 3500cm^{-1} (very broad).

In contrast, when **A** was reacted with sodium amide then treated with isopropyl bromide, it gave **E**, a constitutional isomer of **B**. When **E** was reacted with hydrogen / Lindlar's catalyst it gave **F**, a constitutional isomer of **C**. Reaction of **F** with aq. alkaline $KMnO_4$, it gave **G**, $C_8H_{18}O_2$, IR: 3500cm^{-1} (very broad) as a single meso compound. In contrast, reaction of **F** with CH_3CO_3H followed by treatment with dilute aqueous acid gave **H** as a pair of enantiomers that were found to be diastereomers of **G**.

When **E** was reacted with sodium in liquid ammonia, it gave **I**, a stereoisomer of **F**. Reaction of **I** with aq. alkaline $KMnO_4$, gave the **H** (as a pair of enantiomers again), while reaction of **I** with CH_3CO_3H followed by treatment with dilute aqueous acid gave **G**.

Reaction of **F** or **I** with ozone followed by a work-up using hydrogen peroxide gave 2-methylpropanoic acid as the only product.

- **What are the structures of A to I ?** (12 marks)
- **What type of isomer is D to G and to H ?** (1 mark)

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

AC / IRH / W05