

THE UNIVERSITY OF CALGARY

FACULTY OF SCIENCE

MIDTERM EXAMINATION

CHEMISTRY 353

MARCH 8th, 2006

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

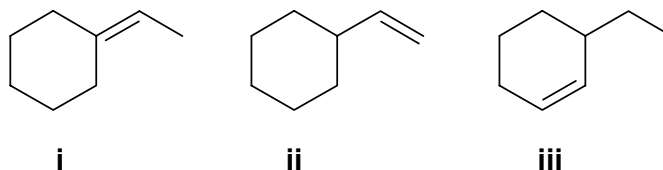
12% ANSWER ANY SIX (6) OF QUESTIONS 1-8.

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

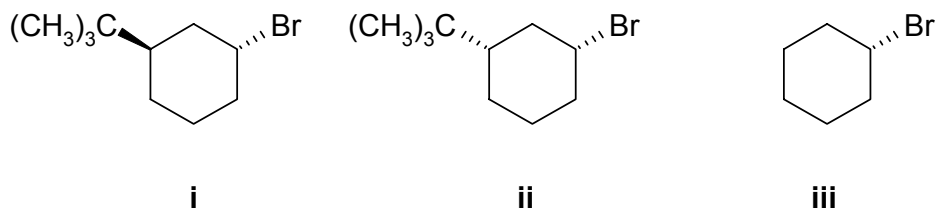
Use the following code to indicate your answers.

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

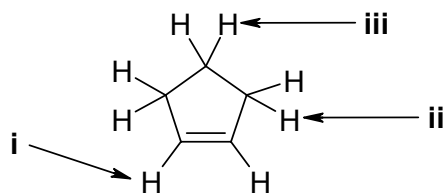
1. The relative number of vinylic hydrogens in each of the following:



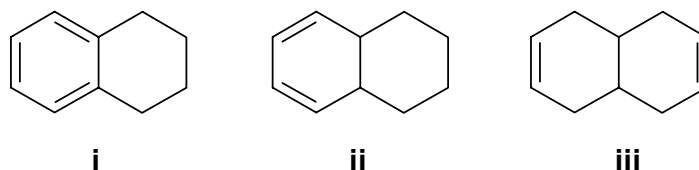
2. The relative reactivity towards potassium *tert*-butoxide of each of the following:



3. The relative bond strength of the indicated C-H bond:



4. The relative heat of hydrogenation (most exothermic to least exothermic) of each of the following:



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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 |

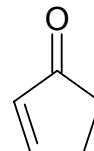
5. The relative reactivity towards 1,3-cyclohexadiene of each of the following:



i

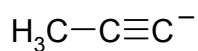


ii



iii

6. The relative base strength of the following:



i

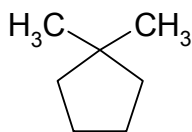


ii

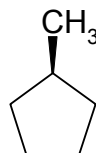


iii

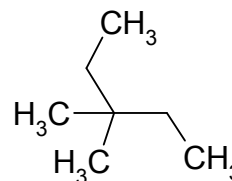
7. The number of possible mono-alkene starting materials that could yield the following on hydrogenation:



i

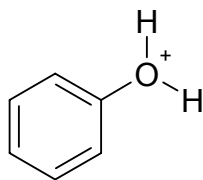


ii

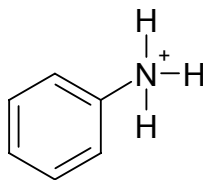


iii

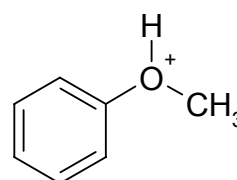
8. The relative acidity of the following:



i



ii



iii

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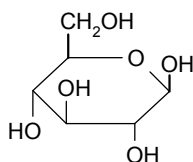
PART 2: LABORATORY

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 contains only one glycosidic bond.
10. Optical rotation is unique to all molecules that contain chiral centres.
11. Glucose (see below) contains an acetal functional group.



12. The rate of a first order reaction is dependant on temperature.

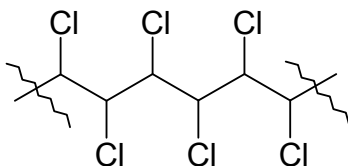
Questions 13-16 are from the experiment about the chemistry of alcohols.

13. Dehydration of alcohols occurs when they are treated with potassium *tert*-butoxide.
14. A positive test for the dehydration of an alcohol results from the alkene product turning a solution of bromine in chloroform red-brown in colour.
15. 1-Phenylethanol can be oxidised by chromium reagents.
16. The Lucas reagent can be used to distinguish 1°, 2° and 3° alcohols containing up to six carbons.

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

17. The following represents a fragment of polyvinyl chloride (PVC):



18. Rubber is an example of a polymer derived from a natural source.
19. Addition of a free-radical source to styrene initiates the polymerization reaction that results in polystyrene.
20. Sodium cyanide is generated when polyacrylonitriles are burned.

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

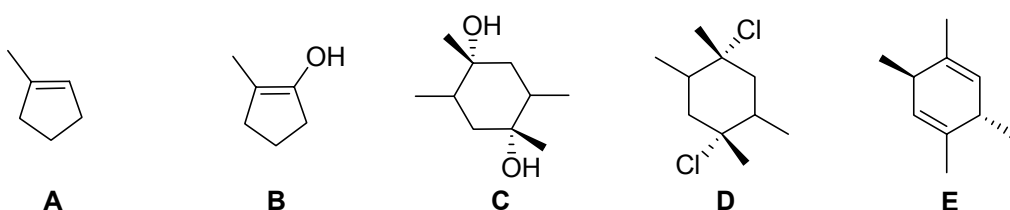
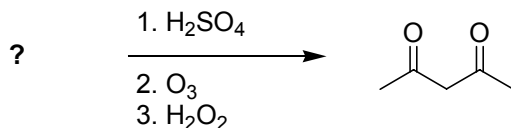
21. In the reaction with the Grignard reagent, carbon dioxide acted as an electrophile.
22. CaCl_2 is an example of an effective drying agent.
23. In a separatory funnel that contains two solutions: diethyl ether and 1M aqueous HCl, the benzoic acid product would be in the ether layer.
24. A rotary evaporator helps to crystallize a solid by reducing the atmospheric pressure.

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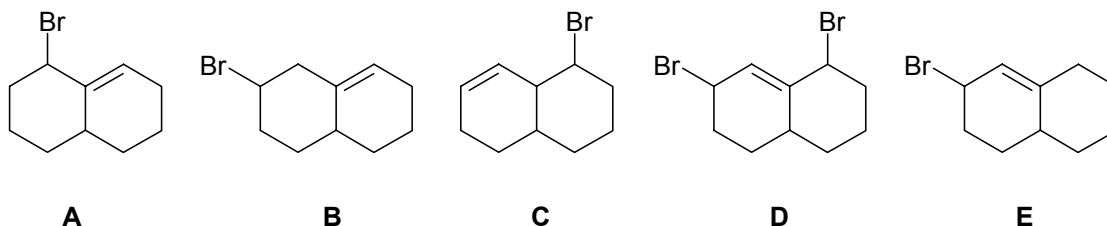
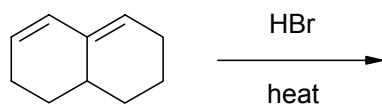
PART 3: STARTING MATERIALS, REAGENTS AND PRODUCTS**12% ANSWER ANY SIX (6) OF QUESTIONS 25-31.**

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.

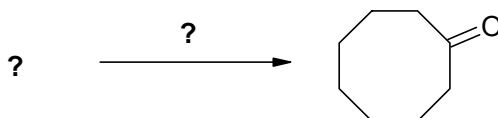
25.



26.



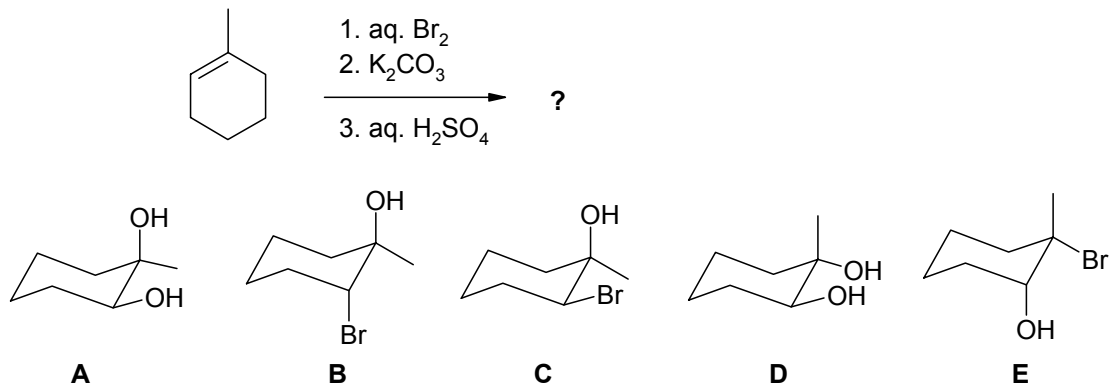
27.



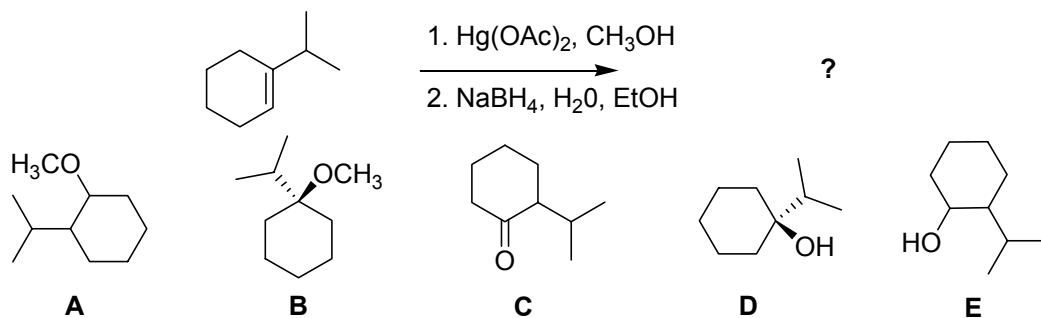
- | | | | | |
|----------|-------------------------------|----------------------|--|--|
| A | 1. Ethyne, NaNH ₂ | 2. 1,6-Dibromohexane | 3. NaNH ₂ | 4. H ₃ O ⁺ , HgSO ₄ |
| B | 1. Propyne, NaNH ₂ | 2. 1-Bromopentane | 3. H ₃ O ⁺ , HgSO ₄ | |
| C | 1. Ethyne, NaNH ₂ | 2. 2,5-Dibromohexane | 3. NaNH ₂ | 4. H ₃ O ⁺ , HgSO ₄ |
| D | 1. Ethyne, NaNH ₂ | 2. 1,5-Dibromohexane | 3. NaNH ₂ | 4. H ₃ O ⁺ , HgSO ₄ |
| E | 1. Ethyne, NaNH ₂ | 2. 1-Bromohexane | 3. NaNH ₂ | 4. H ₃ O ⁺ , HgSO ₄ |

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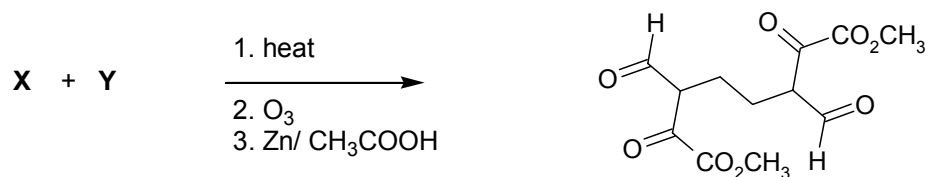
28.



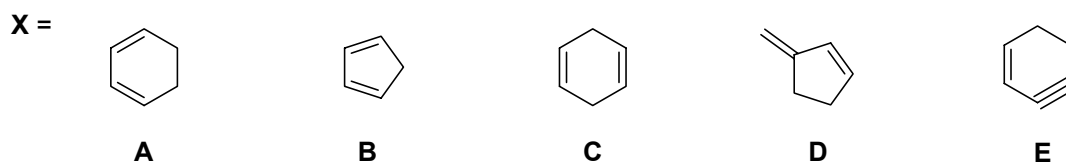
29.



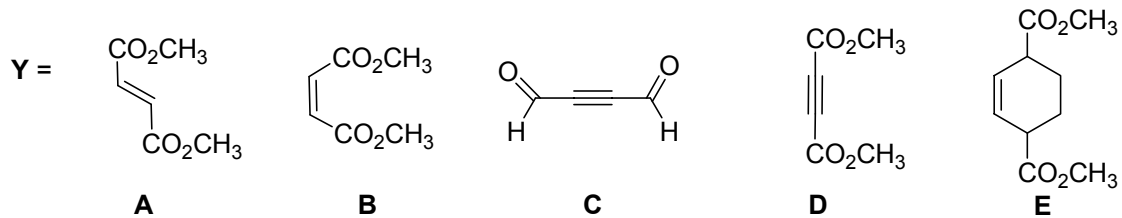
Questions 30 and 31 both apply to the following reaction scheme:



30.



31.



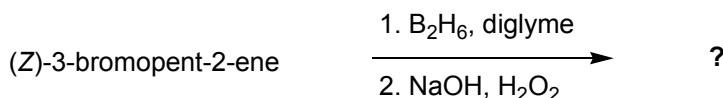
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PART 4: REGIOCHEMISTRY and STEREOCHEMISTRY OF REACTIONS

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

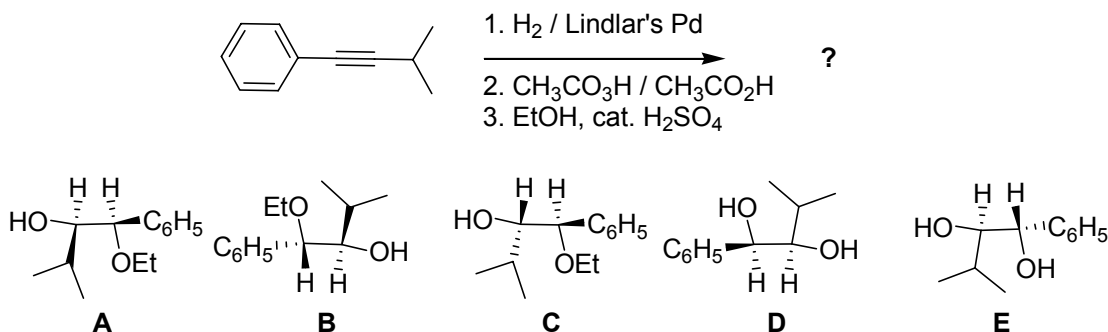
For each of the questions 32-37, select the structure required to complete the reaction shown. If two products are equally abundant, then you must indicate both for full marks. If two starting materials will give the same product, then you must indicate both for full marks. In order to indicate more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

32.

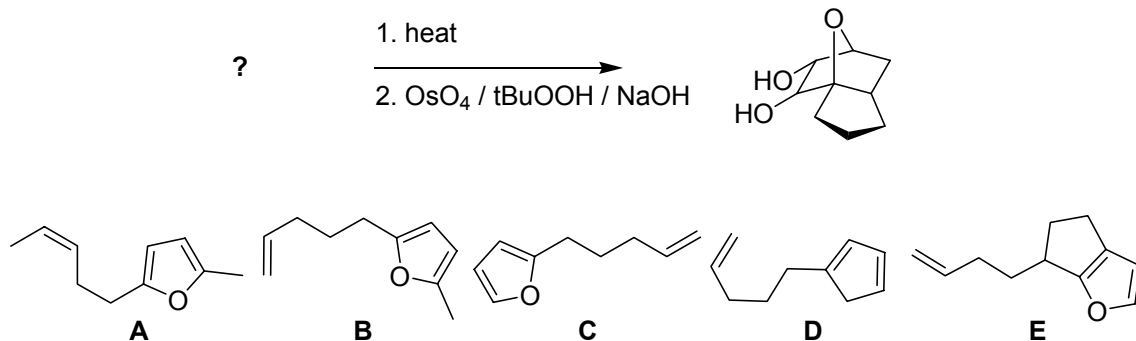


- A (2R,3S)-3-bromopentan-2-ol
 B (2S,3S)-3-bromopentan-2-ol
 C 3-bromopentan-3-ol
 D (2S,3R)-3-bromopentan-2-ol
 E (2R,3R)-3-bromopentan-2-ol

33.

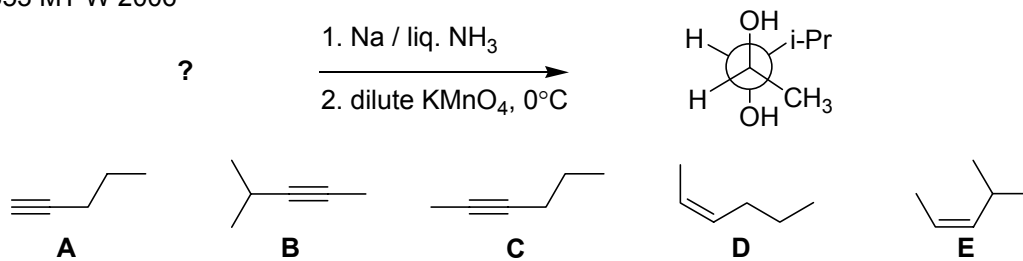


34.

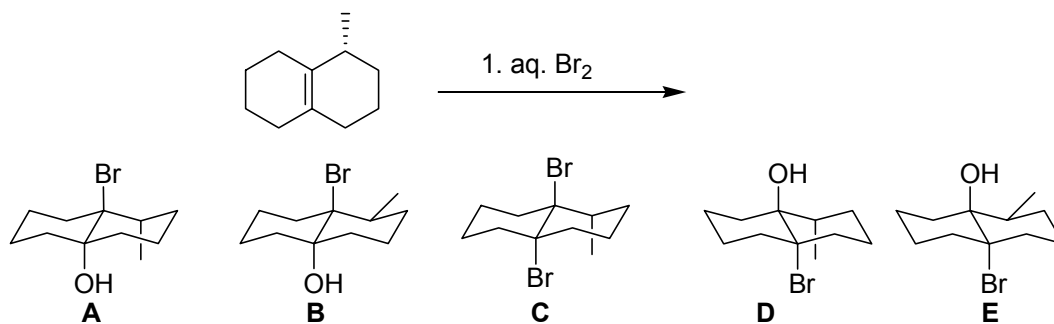


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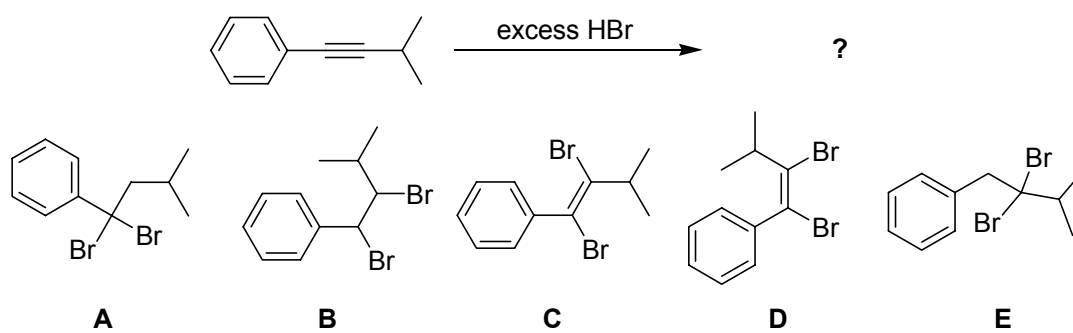
35.



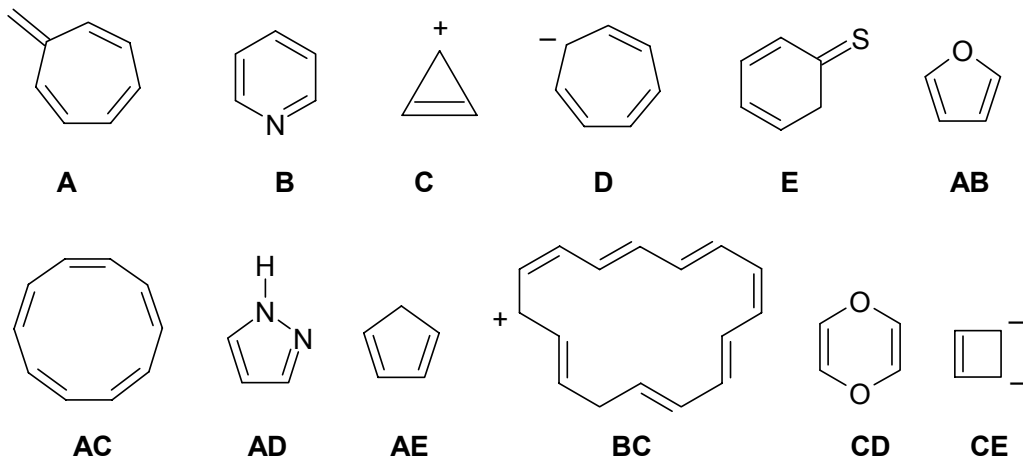
36.



37.



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PART 5: AROMATICITY AND RESONANCE14% **ANSWER ANY SEVEN (7) of the questions 38 - 45.**

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

38. An ionic molecule that is aromatic as drawn with 6 π -electrons.
39. A non-aromatic, uncharged heterocycle.
40. A hydrocarbon molecule that is non-aromatic as drawn, but reacts readily with H^+ to give an aromatic carbocation.
41. Not aromatic as drawn, but has an aromatic tautomer.
42. Of the aromatic heterocycles, which would be the strongest base?
43. An ionic molecule that is not fully conjugated.
44. A molecule that readily undergoes a Diels-Alder reaction and has an aromatic conjugate base.
45. A fully conjugated molecule that obey's the Hückel rule, but is not aromatic.

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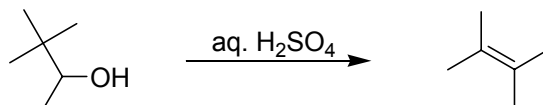
PART 6: MECHANISMS

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

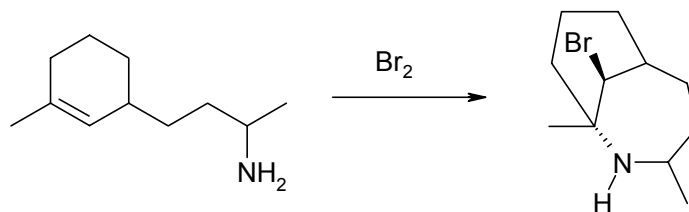
WRITE YOUR ANSWER IN THE BOOKLET PROVIDED

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

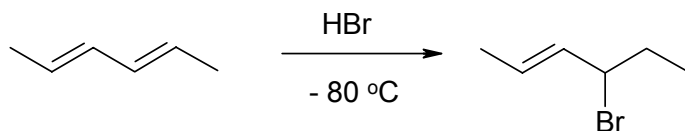
A. Show the mechanism for the following reaction sequence:



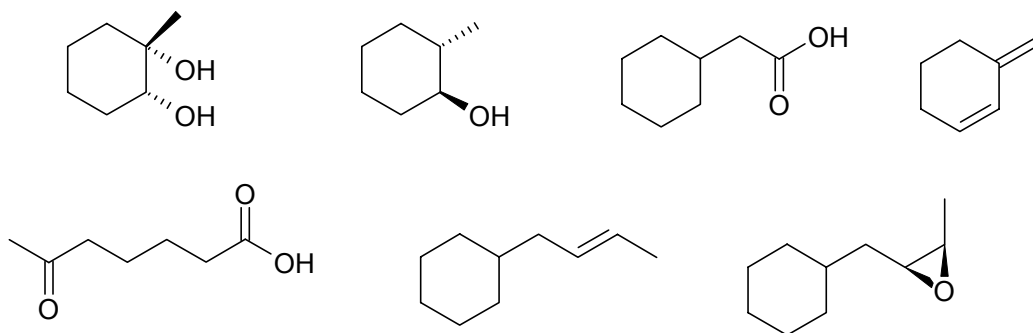
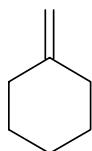
B. Show the mechanism for the following reaction and rationalise the regiochemistry:



C. Show the mechanism for the following, **briefly** explain why, even in the presence of excess HBr, the mono-substituted product is the major product from this reaction:



CONTINUED -->

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 3 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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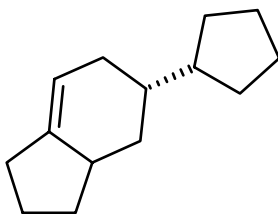
PART 8: STRUCTURE DETERMINATION**13% WRITE YOUR ANSWER IN THE BOOKLET PROVIDED**

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

A and **B** are constitutional isomers with no chiral centres and the molecular formula C_7H_{12} . **A** reacts with HBr to give the achiral molecule **C** ($C_7H_{13}Br$) as the major product. When **A** is reacted with BH_3 , followed by aqueous H_2O_2 / OH^- it yields a pair of isomers **D** and **E** as the two major products. When **C** is treated with potassium *tert*-butoxide, **F** (C_7H_{12}) is the major product. When **F** is treated with ozone, followed by Zn in the presence of water, cyclohexanone is one of the isolated products.

When **B** is treated with *n*-bromosuccinimide, the achiral molecule **G** ($C_7H_{11}Br$) is the major product. When **G** is treated with potassium *tert*-butoxide, **H** (C_7H_{10}) is the major product. When **B** is reacted with BH_3 , followed by aqueous H_2O_2 / OH^- it yields **I**.

When **B** and **H** are heated together in a sealed tube, the following product is isolated:



- What are the structures of **A** to **I** ? (12 marks)
- What type of isomer is **D** in relation to **E** ? (1 mark)

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