

THE UNIVERSITY OF CALGARY

FACULTY OF SCIENCE

FINAL EXAMINATION

CHEMISTRY 353

April 29th, 2003

Time: 3 Hours

PLEASE WRITE YOUR NAME, STUDENT I.D. NUMBER ON THE **COMPUTER ANSWER SHEET** AND THE **BOOKLET** FOR THE WRITTEN ANSWER QUESTIONS.

READ THE INSTRUCTIONS CAREFULLY

The examination consists of Parts 1 - 10, each of which should be attempted. Note that some Parts provide you with a choice of questions, *e.g.* answer 5 out of 6. These will be graded in order the answers appear until the required number have been completed, regardless of whether they are right or wrong.

Parts 1 - 7 will be computer graded, and only Parts 8, 9 and 10 are to be answered in the booklet. Parts 1 - 7 consist of a series of multiple choice questions numbered 1 - 53 which are to be answered on your 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.

A periodic table with atomic numbers and atomic weights and tables of spectroscopic data are provided at the end of the examination paper.

Molecular models are permitted during the exam; calculators are also permitted, but NOT programmable calculators.

Value

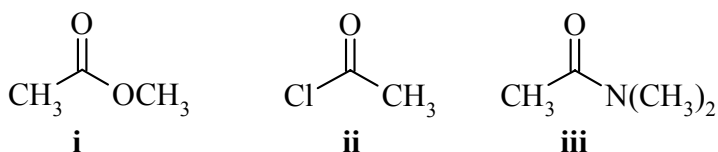
PART 1: RELATIVE PROPERTIES**9% ANSWER ANY SIX (6) OF QUESTIONS 1-10.**

Arrange the items in questions **1-10** in **DECREASING ORDER** (*i.e.* greatest, most etc. first) with respect to the indicated property.

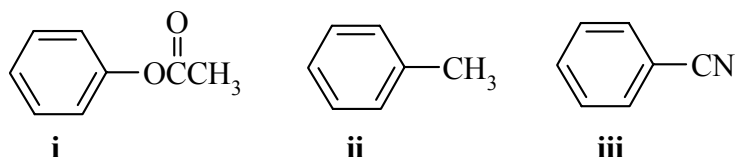
Use the following code to indicate your answers:

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

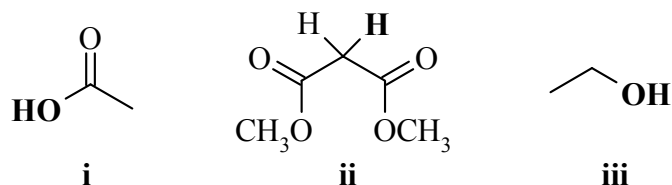
1. The relative rate of hydrolysis by H₂O of each of the following:



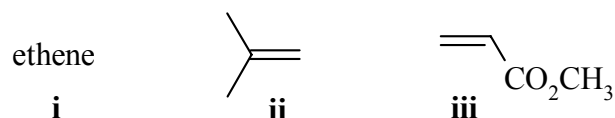
2. The relative rate of reaction of t-butylchloride / AlCl₃ with each of the following:



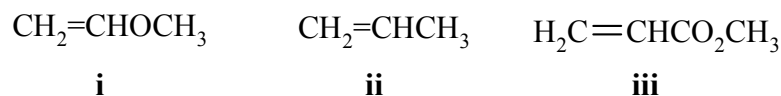
3. The relative acidity of the indicated **H** in each of the following:



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



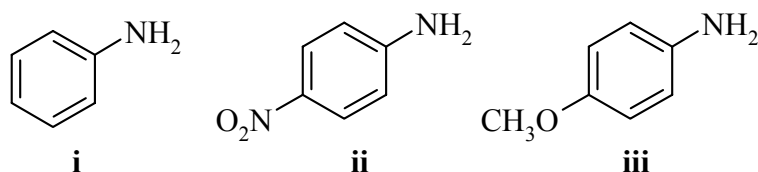
5. The relative reactivity of each of the following towards hydration with aqueous H₂SO₄ :



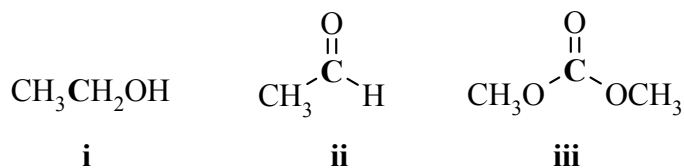
Use the following code to indicate your answers:

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

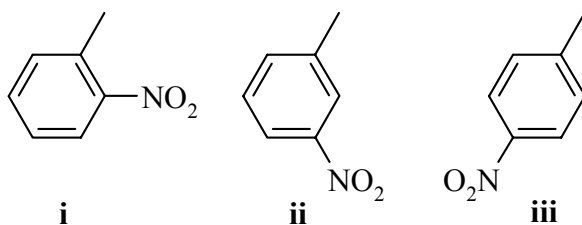
6. The relative basicity of the following :



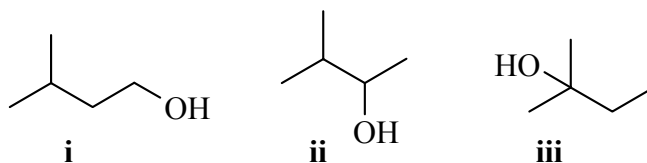
7. The relative oxidation state of the C atom in the following :



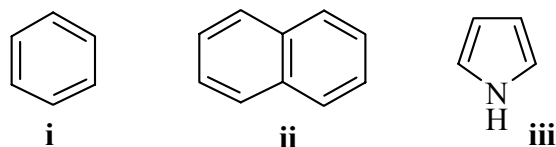
8. The relative yield of the following from the reaction of methylbenzene with HNO₃ / H₂SO₄ :



9. The yield of the following products from the reaction of BH₃ then aq. NaOH / H₂O₂ with 3-methyl-1-butene :



10. The resonance energies of each of the following:



Value

PART 2: LABORATORY**8% ANSWER ALL EIGHT (8) OF THE QUESTIONS 11-18.**

Some answers **MAY** require that you fill in **MORE** than one option.

Stu Dent had unknown **#0001**, which was a colourless liquid. He measured the boiling point to be 233-235°C (uncorrected). The IR and H-nmr of **#0001** are provided on the following page. Stu carried out a series of chemical tests on **#0001** the results of which are shown in the table below. Stu also isolated a liquid product, **STU-A**, from the dichromate test on **#0001**. The results of chemical test on **STU-A** are also shown in the table below. Stu decided to make an oxime as his derivative by reacting **#0001** with hydroxylamine, NH_2OH . The oxime, **STU-B** was isolated and the melting point measured as 58°C.

Chemical Test	Observations for #0001	Observations for STU-A
Water solubility	Insoluble	Very slightly soluble
5% NaHCO_3	Insoluble	Partially soluble
5% NaOH	Insoluble	Soluble
5% HCl	Insoluble	Insoluble
Lucas	No noticeable change	No noticeable change
2,4-Dinitrophenylhydrazine	Red precipitate formed	Orange solution
Iodoform	No visible reaction	No visible reaction
Ferric Chloride	No significant colour change	No significant colour change
Dichromate	Changed from orange to green	No noticeable change

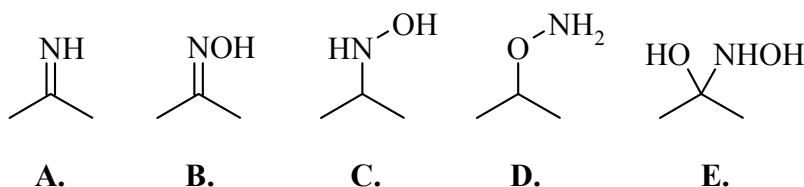
11. The corrected boiling point for unknown **#0001** should be approximately:

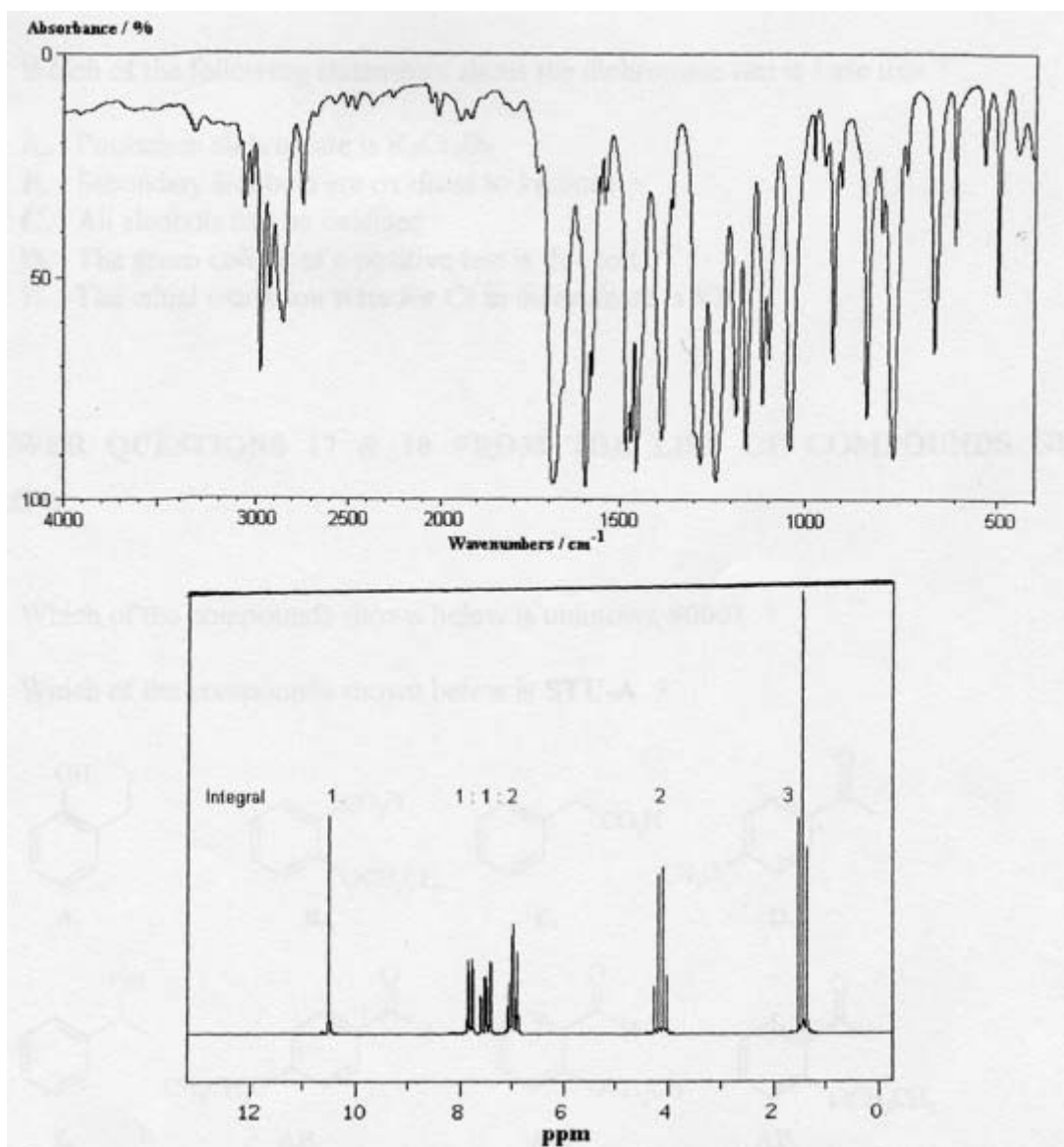
- A 222°C B 227°C C 234°C D 239°C E 248°C

12. Based on the chemical tests *alone* on unknown **#0001** which of the following statements is / are true ?

- A. The unknown could be a phenol
 B. The unknown could be a tertiary alcohol
 C. The unknown could be an aldehyde BUT NOT a ketone
 D. The unknown could be an aldehyde OR a ketone
 E. The unknown could be an carboxylic acid

13. Which of the following is an oxime ?





14. Based on the spectral data *alone* on unknown #0001 which of the following statements is / are true ?
- A. The unknown contains an ethoxy group
 - B. The unknown contains an alcohol
 - C. The H-nmr peak at 10.5 ppm could be an aldehyde CHO group
 - D. The H-nmr peaks at 6.8-8 ppm indicate a monosubstituted benzene
 - E. The band at 1690cm⁻¹ in the IR indicates a carbonyl group
15. Which of the following statements about STU-A is / are true ?
- A. STU-A contains an alcohol functional group
 - B. STU-A contains a C=O group
 - C. STU-A could be an aldehyde or a ketone
 - D. STU-A is a carboxylic acid
 - E. STU-A is an aromatic compound

Value

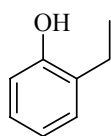
16. Which of the following statements about the dichromate test is / are true ?

- A. Potassium dichromate is $K_2Cr_2O_7$
- B. Secondary alcohols are oxidised to ketones
- C. All alcohols can be oxidised
- D. The green colour of a positive test is due to Cr^{3+}
- E. The initial oxidation state for Cr in dichromate is VII

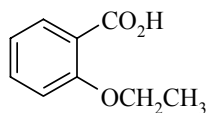
ANSWER QUESTIONS 17 & 18 FROM THE LIST OF COMPOUNDS GIVEN BELOW.

17. Which of the compounds shown below is unknown #0001 ?

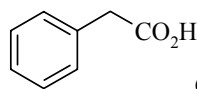
18. Which of the compounds shown below is STU-A ?



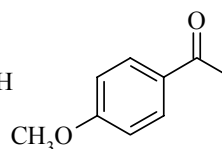
A.



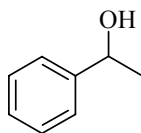
B.



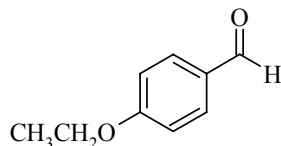
C.



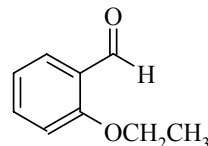
D.



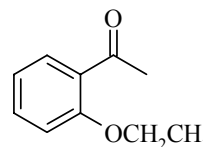
E.



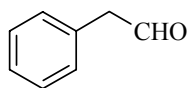
AB.



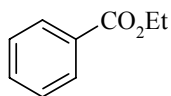
AC.



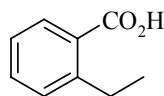
AD.



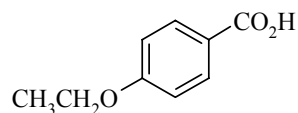
AE.



BC.

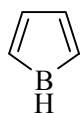
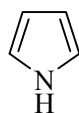
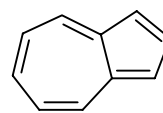
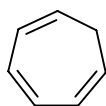
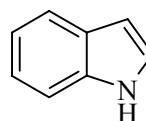
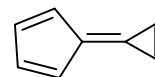


BD.



BE.

Value

PART 3: AROMATICITY AND RESONANCE**9% ANSWER ANY SIX (6) of the questions 19-25.****A****B****C****D****E****AB****AC****AD****AE****BC**

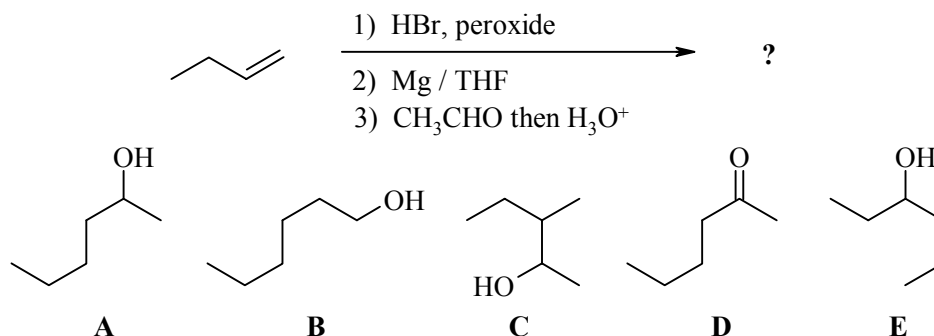
For each of the questions **19-25** select a **single compound** from the list above that is **best** described as:

19. An aromatic system where $n = 2$ in the Huckel rule.
20. A non-aromatic, conjugated triene.
21. An anti-aromatic system.
22. A non-conjugated system.
23. A heterocyclic aromatic system that also has an aromatic conjugate acid.
24. Non-aromatic as drawn but has an aromatic conjugate base.
25. Non-aromatic as drawn but has an important aromatic resonance structure.

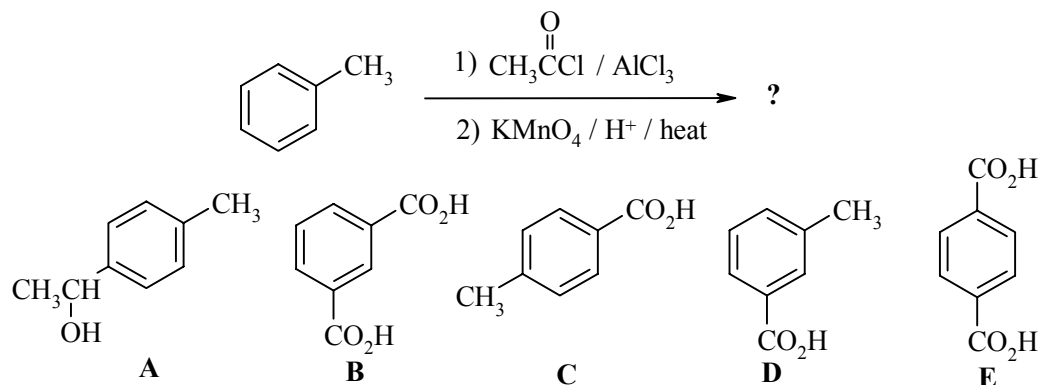
Value

PART 4: PRODUCTS OF SYNTHESIS**10% ANSWER ANY FIVE (5) OF QUESTIONS 26-32.**For each of the questions **26-32** identify the **major product** obtained from each of the reaction sequences shown by selecting from the list of possible products provided.

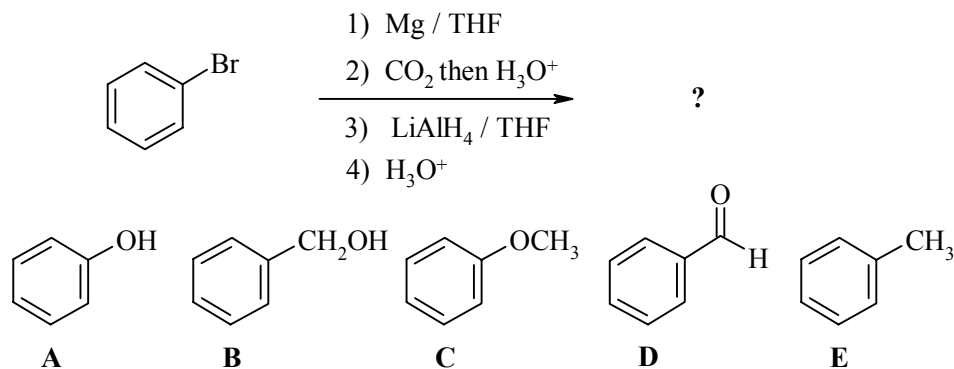
26.



27.



28.

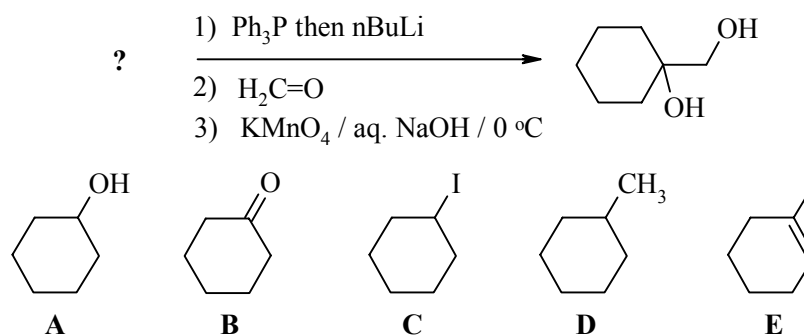


PART 5: STARTING MATERIALS FOR SYNTHESIS

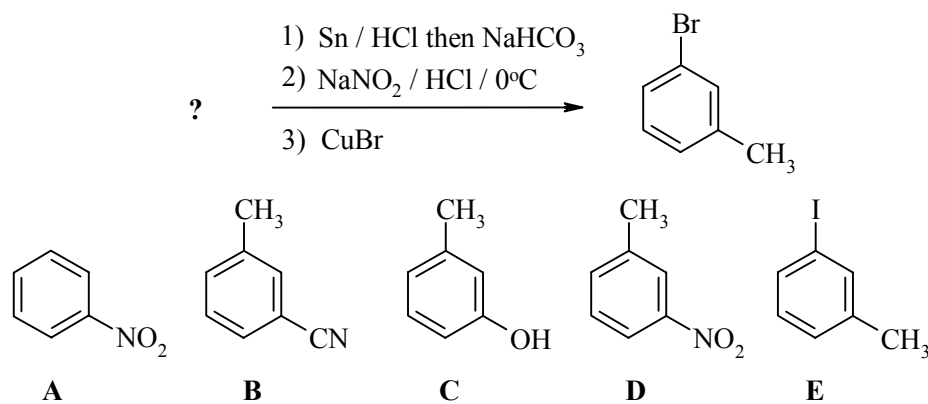
10% ANSWER ANY FIVE (5) OF QUESTIONS 33-39.

For each of the questions **33-39**, choose the starting material from the selection provided that gives the product indicated via the transformations shown.

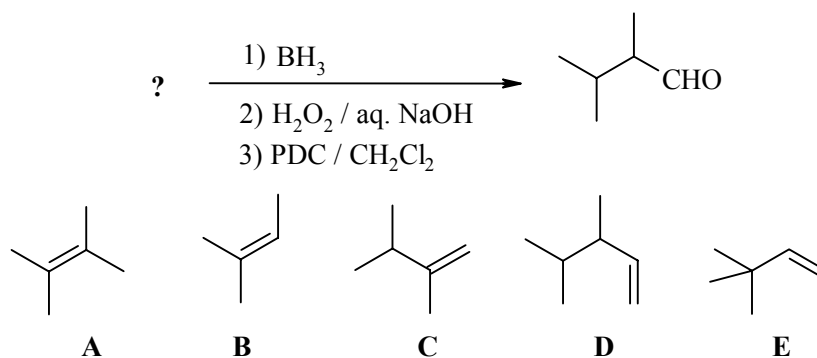
33.



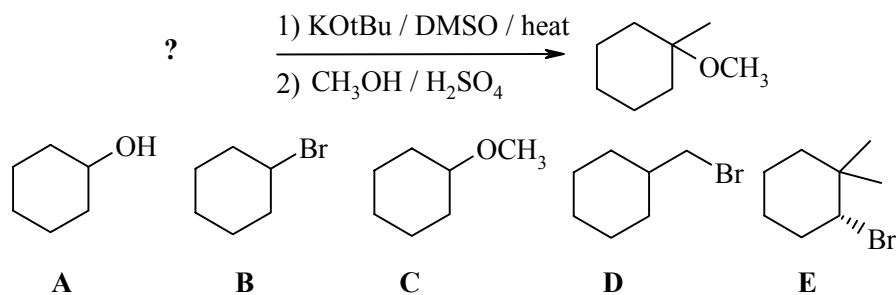
34.



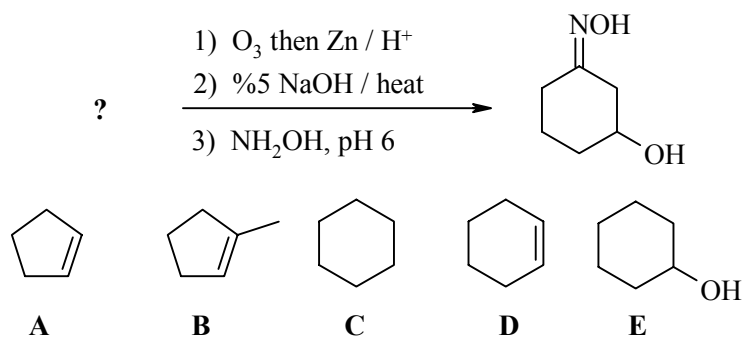
35.



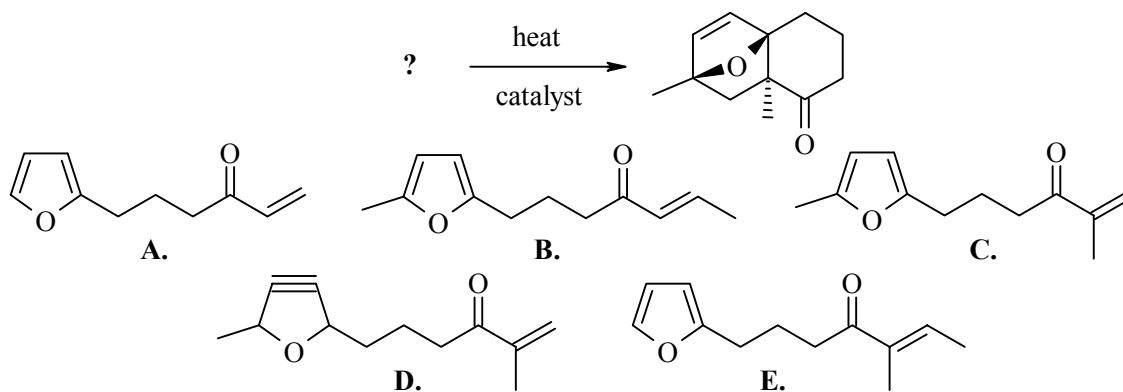
36.



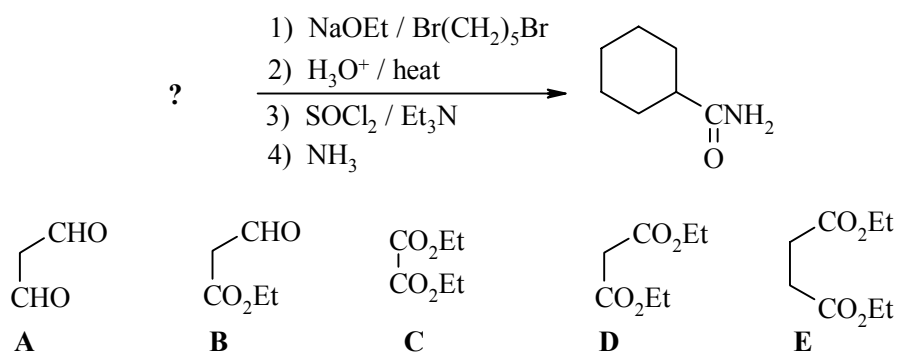
37.



38.



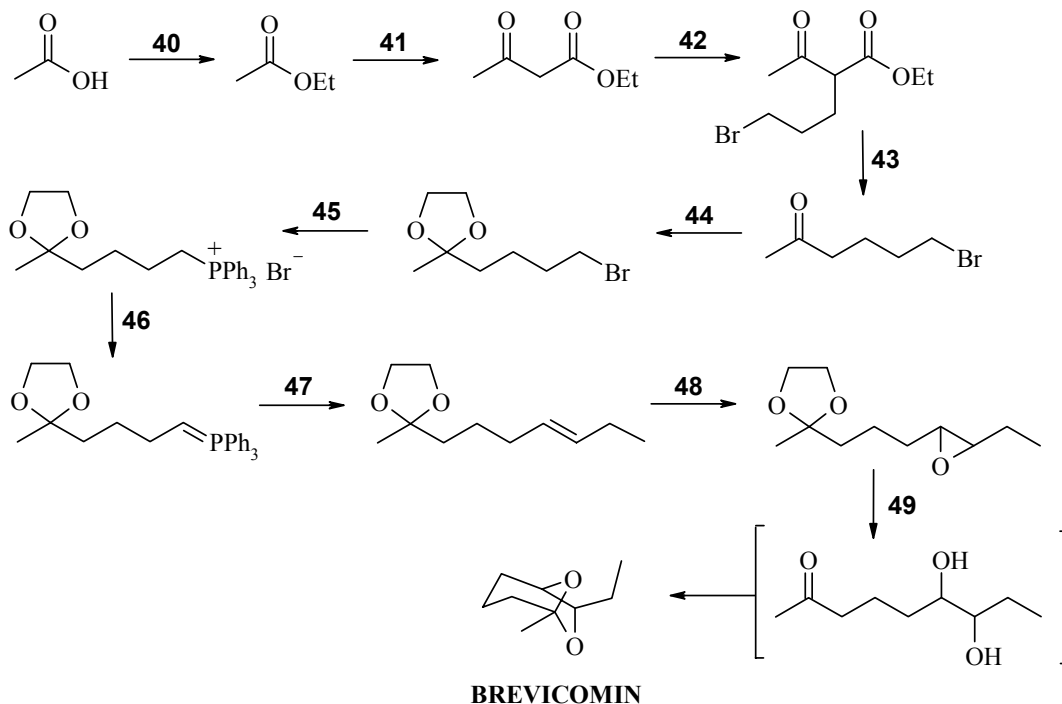
39.



PART 6: REAGENTS FOR SYNTHESIS

10% ANSWER ALL OF THE QUESTIONS 40 - 49

The following reaction scheme shows a possible synthesis of BREVICOMIN, a pheromone of the Western Pine Beetle. From the list of reagents provided in the table below, select the best reagent combination to carry out each of the reactions required at each numbered step.



- | | |
|---|---|
| A. $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Li} / \text{THF}$ | AE. $\text{CH}_3\text{CH}_2\text{CH}_2\text{MgBr} / \text{THF}$ then H_3O^+ |
| B. $\text{CH}_3\text{CH}=\text{CH}_2$ | BC. $\text{H}_3\text{O}^+ / \Delta$ |
| C. $\text{CH}_3\text{CO}_2\text{H}$ | BD. $\text{Conc. H}_2\text{SO}_4 / \Delta$ |
| D. $\text{CH}_3\text{CO}_3\text{H}$ | BE. NaOEt then $\text{Br}(\text{CH}_2)_3\text{Br}$ |
| E. $(\text{CH}_3)_2\text{C}=\text{O} / \text{H}^+$ | CD. $\text{NaOEt} / \text{EtOH}$ |
| AB. $\text{CH}_3\text{CH}_2\text{CHO}$ | CE. LiAlH_4 then H_3O^+ |
| AC. $\text{PBr}_3 / \text{Et}_3\text{N}$ | DE. $\text{HOCH}_2\text{CH}_2\text{OH} / \text{H}^+$ |
| AD. PPh_3 | ABC. $\text{EtOH} / \text{H}^+ / \text{heat}$ |

Value

PART 7: EXPLANATION OF PHENOMENA**8% ANSWER ALL OF THE QUESTIONS 50 - 53.**Choose the **SINGLE** explanation that **BEST** describes the phenomenon indicated.

50. When an internal alkyne reacts with excess HCl, the product is a geminal dichloride because:

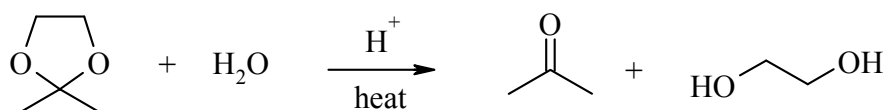
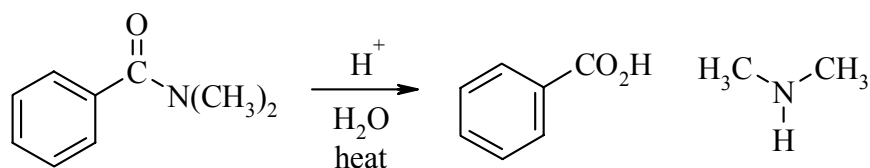
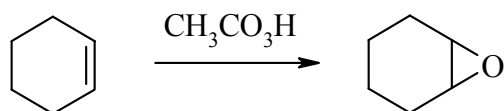
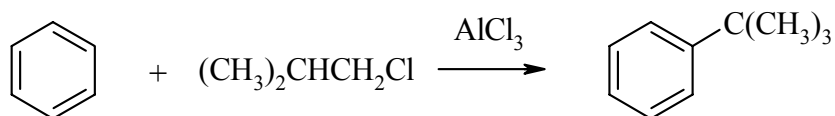
- A. This is a radical halogenation and proceeds via the most stable radical.
- B. A carbocation rearrangement occurs.
- C. Halogens can stabilise carbocations by resonance.
- D. Chlorine adds forming a cyclic halonium ion that is opened when chloride attacks.
- E. The reaction shows anti-Markovnikov selectivity.

51. Pyrrole has a $pK_a = -3.8$ whereas pyridine has a $pK_a = 5.2$ with respect to their conjugate acids because:



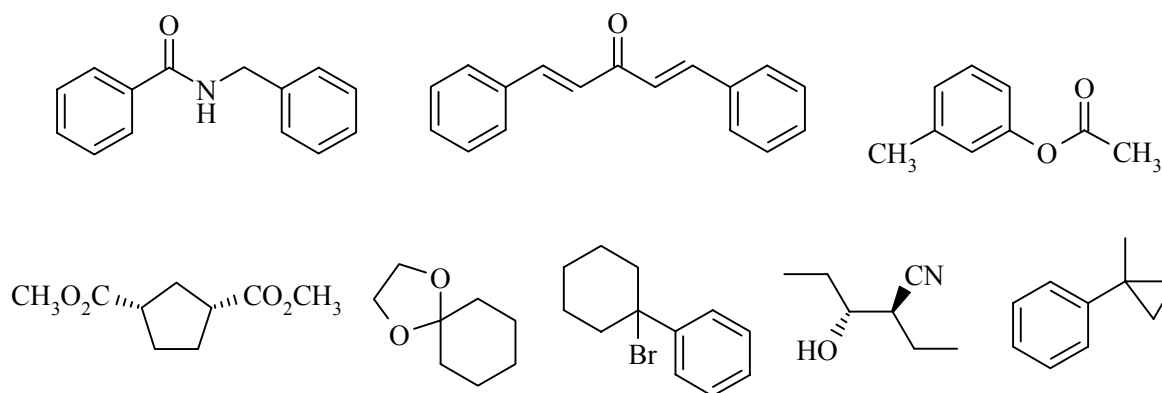
- A. Pyrrole and pyridine are both aromatic.
 - B. Pyridine and its conjugate acid are aromatic.
 - C. Pyrrole and its conjugate acid are aromatic.
 - D. Pyridine has an aromatic conjugate acid while pyrrole doesn't.
 - E. The N atom in pyridine is sp^2 hybridised.
52. When amides react with an acid, they protonate on the oxygen rather than the nitrogen because:
- A. O is more electronegative than N.
 - B. O atoms are usually more basic than N atoms in similar environments.
 - C. The O atom can be considered to be sp^2 hybridised.
 - D. There is more resonance stabilisation when O is protonated compared to N.
 - E. There are more lone pairs on the O atom.
53. In general, aldehydes are more reactive towards nucleophiles than ketones because:
- A. Ketones are more electrophilic than aldehydes
 - B. The aldehydic H is an electron withdrawing group.
 - C. Alkyl groups are larger than H atoms and are electron donating.
 - D. Alkyl groups are larger than H atoms and are electron withdrawing.
 - E. The reaction is controlled by simple steric effects.

Value

PART 8: MECHANISM**12% ANSWER ANY THREE (3) OF QUESTIONS A - D****WRITE YOUR ANSWER IN THE BOOKLET PROVIDED****Use curly arrow mechanisms to show the mechanisms for ANY THREE (3) of the following transformations. NO other reagents are required.****A.****B.****C.****D.**

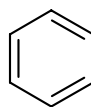
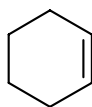
Value**PART 9: TOTAL SYNTHESIS****WRITE YOUR ANSWERS IN THE BOOKLET PROVIDED**

12% Design an efficient synthesis for any **THREE (3)** of the following target molecules using any of the starting materials and reagents given in the accompanying list. Show the product of each step and clearly identify the reagents.

DO NOT SHOW MECHANISMS.

Permitted Starting Materials and Reagents

- Any inorganic materials
- Any organic compounds with no more than 3 carbons
- triphenyl phosphine
- MCPBA
- Any of the following:



PART 10: STRUCTURE DETERMINATION

12% WRITE YOUR ANSWERS IN THE BOOKLET PROVIDED

An achiral compound, **A**, 88.162% C and 11.839% H, was heated in a sealed tube with ethene at 200 °C to provide **B**, C₇H₁₂ that was found to decolourise Br₂ in CCl₄. When **B** was reacted with BH₃ with the H₂O₂ / aq. NaOH work-up, **C**, C₇H₁₄O was obtained as a pair of enantiomers. Subsequent reaction of **C** with pyridinium chlorochromate (PCC) in CH₂Cl₂ gave racemic **D**, C₇H₁₂O which gave a yellow precipitate when reacted with 2,4-dinitrophenylhydrazine.

When **D** was reacted methyl magnesium bromide followed by a dilute aqueous acid work-up it gave **E**, C₈H₁₆O as a mixture of 4 stereoisomers. Reaction of **E** with conc. H₂SO₄ / heat produced **F**, C₈H₁₄, a single compound as the major product. Reaction of **F** with O₃ followed by work-up with Zn / CH₃CO₂H gave octan-2,7-dione.

When **D** was reacted with the ylid formed from the reaction of Ph₃P, CH₃I and n-BuLi, **G**, an isomer of **F** was formed as a racemic mixture.

Catalytic hydrogenation of **F** with H₂ / Pd gave 1,2-dimethylcyclohexane as a single compound.

In contrast, reaction of **G** with H₂ / Pd gave 1,2-dimethylcyclohexane as a pair of enantiomers.

Examination of the ¹³C-nmr spectra showed the following numbers of peaks : **A** = 5, **B** = 7, **C** = 7, **D** = 7, **E** = 8, **F** = 4, **G** = 8.

Examination of the IR spectra showed the following important bands (cm⁻¹) : **A** 1600, **C** 3350 (broad), **D** 1712, **E** 3340 (broad), **G** 1600.

What are the structures **A** - **G** ?

THE END