

**UNIVERSITY OF SWAZILAND  
FINAL EXAMINATION 2005**

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**TITLE OF PAPER** : Organic Chemistry

**COURSE NUMBER** : C303

**TIME** : Three Hours

**INSTRUCTIONS** : Answer any **FOUR** questions. Each question carries **25** marks.

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**QUESTION 1**

- (a) Briefly explain the following terms and give examples to illustrate:
- (i) Syn-addition
  - (ii) Anti-elimination (5)
- (b) What is anchimeric assistance? Illustrate your answer with the hydrolysis of (S)-2-bromopropanoic acid in presence of
- (i) dilute sodium hydroxide and silver oxide
  - (ii) concentrated sodium hydroxide (10)
- (c) Write the mechanism for each of the following reactions. In each case write the Fischer projection of the product(s) and state with reasons whether the product is optically active or not:
- (i) chlorination of cis-2-butene
  - (ii) chlorination of trans-2-butene (10)

**QUESTION 2**

- (a) Explain with appropriate structures and mechanism why E2 reaction of 1-bromo-1, 2-diphenylpropane is said to be both stereoselective and stereospecific. (10)
- (b) Write the mechanism for each of all the possible products of the following reactions:
- (i) 3,3-Dimethyl-1-butene with hydrogen bromide
  - (ii) 1-Bromo-2,2-dimethylpropane with ethanol
  - (iii) Dehydration of 2-methyl-1-butanol with concentrated sulphuric acid
  - (iv) Benzene with 1-chlorobutane in presence of aluminium chloride (15)

**QUESTION 3**

- (a) Outline all steps in the following transformations:
- (i) Conversion of 2,3-dimethyl-2,3-butanediol (pinacol) to 3,3-

dimethyl-2-butanone (pinacolone).

(ii) Conversion of propanoic acid to butanoic acid. (10)

(b) Outline all steps in the synthesis of

(i) 2-methylpentanoic acid starting with ethylmalonate.

(ii) aspartic acid  $[\text{HOOCCH}_2\text{CH}(\text{NH}_3^+)\text{COO}^-]$  starting with ethylbromomalonate  $[\text{C}_2\text{H}_5\text{OOCCH}(\text{Br})\text{COOC}_2\text{H}_5]$  (15)

#### QUESTION 4

(a) (i) How would you use  $^1\text{H}$  NMR to distinguish between ethanol and dimethylether?

(ii) Name and write the structures of the three isomeric ethers of  $\text{C}_4\text{H}_{10}\text{O}$ .

(iii) State how many signals will arise in the  $^{13}\text{C}$  nmr spectrum of each compound named. (8)

(b) What is a base peak in the mass spectrum of a compound? (2)

(c) Predict the mass to charge ratio and structure of the base peak in the mass spectrum of each of the following compounds:

(i) 2-Methylpentane

(ii) 4-Ethyl-4-octanol (5)

(d) Explain each of the following phenomena:

(i) The absorption maximum of aniline suffers a blue shift when aniline is dissolved in hydrochloric acid.

(ii) The infra red absorption spectrum of a solution of an alcohol in  $\text{CCl}_4$  showed a very sharp peak in the  $3590 - 3650\text{cm}^{-1}$  region while the same alcohol gave a broad band in the  $3200 - 3550\text{cm}^{-1}$  region when the spectrum was run in nujol.

(iii)  $^1\text{H}$  NMR spectra of most organic compounds are usually measured in the

presence of tetramethylsilane. (10)

### **QUESTION 5**

- (a) What is an aromatic compound and how does it differ with a nonaromatic one? (5)
- (b) Give detailed experimental evidences with essential structures for the mechanism of nucleophilic aromatic substitution through benzyne? (20)

### **QUESTION 6**

- (a) Explain the following terms and where possible illustrate with an example:
- (i) Concerted reaction
  - (ii) Electrocyclic reaction
  - (iii) Cycloaddition reaction
  - (iv) Conrotatory motion
- (12)
- (b) Give four characteristics features of electrocyclic reactions (4)
- (c) Give the names and structures of the products of the following reactions:
- (i) Thermal electrocyclic reaction of cis-3,4-dimethyl cyclobutene
  - (ii) Thermal electrocyclic reaction of trans,cis,cis-2,4,6-octatriene
  - (iii) Addition of 1,3-butadiene to propenal at 100<sup>o</sup> C (9)

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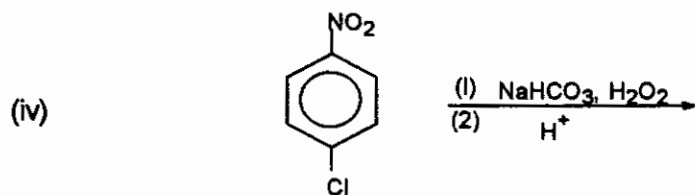
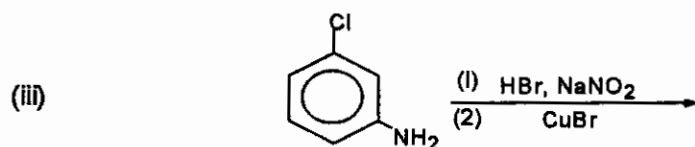
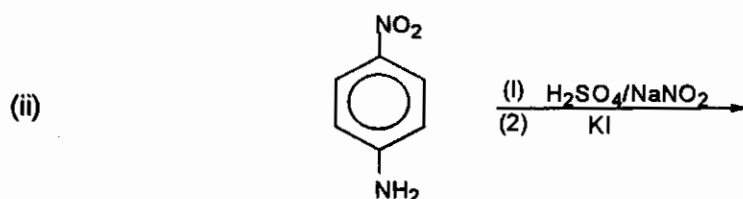
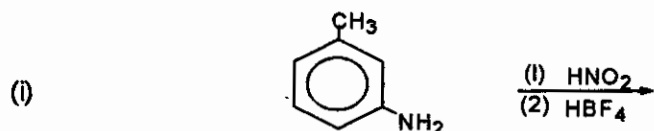
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**QUESTION 1**

- (a) Write the three isomeric ethers with the molecular formula  $C_4H_{10}O$  : name them and state how many signals will arise in the  $^{13}C$  nmr spectrum of each. (12)
- (b) (i) How many ions would you expect in the mass spectrum of 2-hexene by  $\beta$ -fragmentation?  
(ii) What are the masses of the ions in (i) above? (6)
- (c) Predict the structure of a compound with molecular formula  $C_7H_8O$  that has  $^1H$  nmr signals at  $\delta = 7.3, 4.4$  and  $3.7$  ppm with relative intensities of 7:2.9:1.4 respectively. (7)

**QUESTION 2**

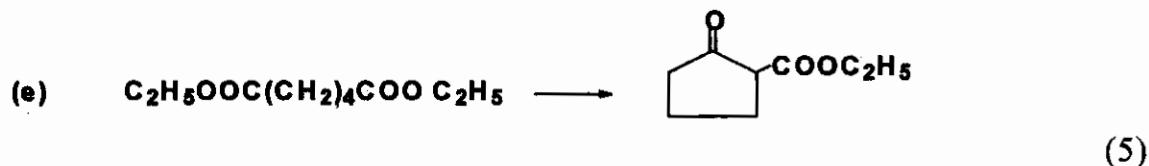
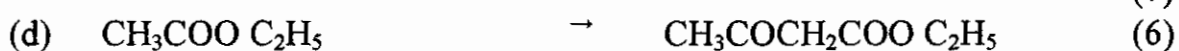
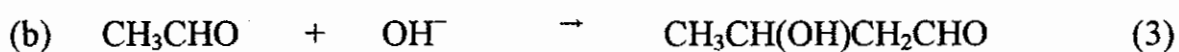
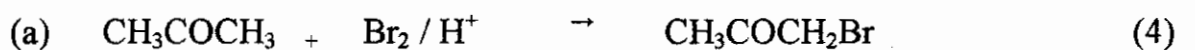
- (a) Write the structure of the product of each step of the following : (16)



- (b) Write all steps involved in the mechanism of nucleophilic aromatic substitution involving Meisenheimer complex. Give the effect that electron-withdrawing groups have on the substitution. (9)

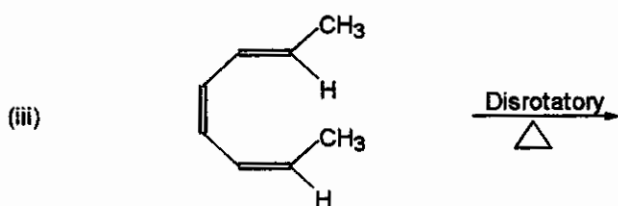
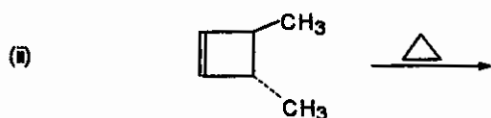
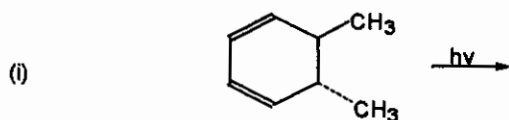
### QUESTION 3

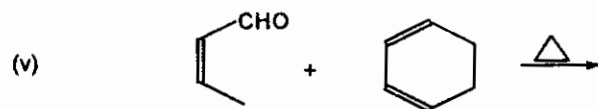
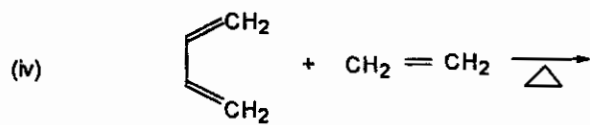
Write the likely steps in the following transformations:



### QUESTION 4

- (a) Write structures and names of the products of the following reactions: (15)





- (b) What is meant by the term “disrotatory motion” in electrocyclic reactions? Illustrate your answer with any diene. (4)
- (c) What is a sigmatropic reaction? Give an example with structures. (3)
- (d) Why is thermal cycloaddition of ethene difficult? (3)

**QUESTION 5**

Write all the possible organic products of each of the following reactions and give a mechanism to explain how each product is formed.

- (a) CH3C(CH3)2CH=CH2 + HI >> (6)
- (b) CH3C(CH3)2CH2Br + C2H5OH (Dilute) >> (4)
- (c) CH3C(CH3)2CH(OH)CH3 + H2SO4 (Concentrated) >> (5)
- (d) CH3CH2CH2CH2CH2Cl + C6H6 (In presence of AlCl3) >> (5)
- (e) (CH3)2C(OH)C(OH)(CH3)2 (glycol) + HNO3 (oxidising agent) >> (5)



**QUESTION 6**

Explain the following reactions with appropriate structures and mechanisms:

- (a) E2 reaction of 1-bromo-1,2-diphenylpropane is both stereoselective and stereospecific

(15)

(b)

Hydrolysis of S-2-bromopropanoic acid with concentrated sodium hydroxide gives R-lactate while hydrolysis in dilute sodium hydroxide in presence of silver oxide gives S-lactate.

(10)