

**UNIVERSITY OF SWAZILAND  
MAIN EXAMINATION 2006**

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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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*You are not supposed to open this paper until permission to do so has been granted by the Chief Invigilator.*

### QUESTION 1

Write down the likely steps in the following transformations:

- (a) Propanone to 3,3-dimethyl-2-butanone (6)
- (b) Phenol to perlon [-CONH(CH<sub>2</sub>)<sub>5</sub>-]<sub>n</sub> (6)
- (c) Ethyl acetoacetate to 3-methyl-2-hexanone (8)
- (d) Ethyl malonate to 4-methyl pentanoic acid (5)

### QUESTION 2

- (a) Explain the following reactions with appropriate structures and mechanisms:
  - (i) Bromination of methyl acetylene is stereoselective and not stereospecific.
  - (ii) Bimolecular elimination reaction of 1-chloro-1,2-diphenylpropane is both stereoselective and stereospecific (15)
- (b) Write the mechanism for the hydrolysis of S-2-chloropropanoic acid with each of the following reagents and indicate the stereochemistry of each product:
  - (i) Concentrated sodium hydroxide
  - (ii) Dilute sodium hydroxide in presence of silver oxide. (10)

### QUESTION 3

- (a) Explain each of the following phenomena with appropriate structures:
  - (i) Aryl halides are generally less reactive than alkyl halides in S<sub>N</sub>1 and S<sub>N</sub>2 reactions
  - (ii) Alkyl halides are less reactive than benzene in electrophilic substitution
  - (iii) Electrophiles usually go to ortho and para positions of the halogen in electrophilic aromatic substitutions of aryl halides. (10)

- (b) Write the mechanism for the conversion of chlorobenzene to aniline through benzyne. (6)
- (c) Describe how  $^{14}\text{C}$ -labeled chlorobenzene has been used to provide experimental evidence that nucleophilic aromatic substitution occurs through a mechanism involving benzyne. (9)

#### QUESTION 4

- (a) Explain the following terms:  
(i) Red shift  
(ii) Chromophore  
(iii) Molar absorptivity (6)
- (b) Ethene, 1,3-pentadiene and 1,4-pentadiene have  $\lambda_{\text{max}}$  223nm, 171nm and 178nm but not arranged in the same order in which the compounds are arranged. Match each compound with its  $\lambda_{\text{max}}$  with reasons. (5)
- (c) Describe briefly four ways by which compounds may be examined in infrared spectrometer. (8)
- (d) Predict the structure of the base peak of each of the following compounds in their mass spectra:  
(i) Octane  
(ii) 2-Methyl pentane (6)

#### QUESTION 5

- (a) Write the four characteristic features of electrocyclic reactions (4)
- (b) Write the structure and name of the product of the addition of 1,3-butadiene with each of the following:  
(i) Maleic anhydride  
(ii) Acrolein  
(iii) p-Benzoquinone (10)

- (c) Write the structure and name of the product of the thermal electrocyclic reactions of each of the following compounds:
- (i) cis-3,4-dimethyl cyclobutene
  - (ii) trans-3,4-dimethyl cyclobutene
  - (iii) trans, cis, trans-2,4,6-octatriene
- (d) What is a disrotatory motion?

(9)

(2)

### QUESTION 6

- (a) Write all the possible organic products of each of the following reactions and give a mechanism to explain how each product is formed.
- (i)  $\text{CH}_3\text{C}(\text{CH}_2)_2\text{CH}=\text{CH}_2$  + HBr
  - (ii)  $\text{CH}_3\text{C}(\text{CH}_3)_2\text{CH}(\text{OH})\text{CH}_3$  +  $\text{H}_2\text{SO}_4$  (concentrated)/Heat
  - (iii)  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$  +  $\text{C}_6\text{H}_6/\text{AlCl}_3$
- (b) Write the mechanism involved in the following transformations:
- (i) Conversion of acetone to methyl acetate in the presence of peracetic acid.
  - (ii) Reaction of 2,2-dimethyl-1-chloropropane with aqueous ethanol

(15)

(10)