

**UNIVERSITY OF SWAZILAND  
MAIN EXAMINATION 2006/07**

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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

- (a) Write the mechanism for each of the following reactions. In each case write the names and Fischer projections of their products. State with reasons whether or not each product is optically active:
- (i) bromination of cis-2-butene
  - (ii) bromination of trans-2-butene (12)
- (b) Write the Fischer projections of products of the following reactions:
- (i) addition of peracetic acid to trans-2-butene
  - (ii) bromination of maleic acid (cis-2-butenedioic acid)
  - (iii) bromination of fumaric acid (trans-2-butenedioic acid) (8)
- (c) Explain with examples enantiospecificity and its importance in biological systems (5)

### QUESTION 2

Write all steps in the mechanism for each of the following reactions:

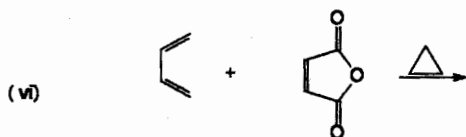
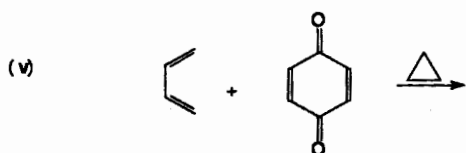
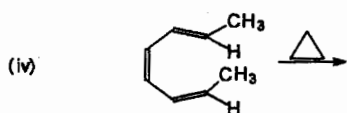
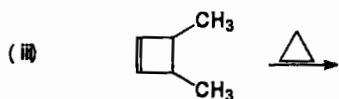
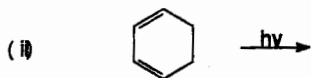
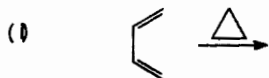
- (a) (i) Conversion of acetone (propanone) to pinacolone (3,3-dimethyl-2-butanone).  
(ii) Conversion of 3-amino-2,3-dimethyl-2-butanol to pinacolone (13)
- (b) Conversion of benzaldehyde to benzilic acid (diphenylhydroxyacetic acid). (12)

### QUESTION 3

- (a) (i) Write the structure of 2-methyl-1,3-cyclohexanedione.  
(ii) Would you expect 2-methyl-1,3-cyclohexanedione to be more or less acidic than cyclohexanone? Explain your answer. (3)
- (b) Outline all steps in the synthesis of  $\alpha$ -methylvaleric acid (2-methylpentanoic acid) starting with ethylmalonate. (10)
- (c) (i) Outline all steps in the synthesis of aspartic acid  $[\text{HOOCCH}_2\text{CH}(\text{NH}_3^+)\text{COO}^-]$  starting with ethylbromomalonate  
(ii) What is the optical property of the aspartic acid produced in (c) (i)? Give reason. (12)

**QUESTION 4**

(a) Write the structures and names of products of the following reactions: (12)



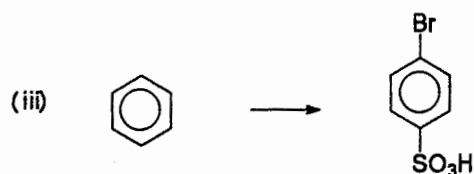
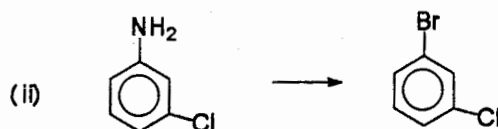
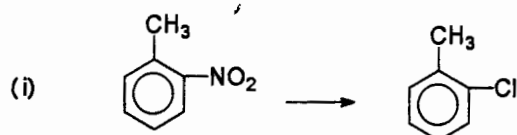
(b) What is meant by the term "disrotatory motion" in electrocyclic reactions? Illustrate your answer with butadiene. (8)

(c) How feasible is thermal cycloaddition of ethene? Give an explanation for your answer. (5)

### QUESTION 5

(a) Write all the steps in the following transformations:

(11)



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

(c) Compare the reactivity of bromobenzene and o-deuteriobromobenzene with the amide ion. What is the implication of their reactivities to the possible mechanism of nucleophilic aromatic substitution? (5)

### QUESTION 6

(a) (i) Write the structures of the isomers of dinitrobenzene.  
(ii) Indicate the equivalent carbon atoms in each structure of dinitrobenzene and the number of signals that will arise in its  $^{13}\text{C}$  nmr spectrum. (9)

(b) Write the ions you would expect in the mass spectrum of 2-hexene by  $\beta$ -fragmentation and their masses. (6)

(c) Predict the structure of a compound with molecular formula  $\text{C}_7\text{H}_8\text{O}$  that has

$^1\text{H}$  nmr signals at  $\delta = 7.3, 4.4$  and  $3.7$  ppm with relative intensities of 7:2.9:1.4 respectively. (7)

- (d) Explain why the absorption maximum of aniline in hydrochloric acid suffers a blue shift. (3)