

**UNIVERSITY OF SWAZILAND
MAIN EXAMINATION 2007/08**

TITLE OF PAPER : Organic Chemistry

COURSE NUMBER : C303

TIME : Three Hours

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

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

QUESTION 1

Explain the following observations with appropriate structures and mechanisms:

- (a) Catalytic reduction of alkynes usually gives mainly cis-products (3)
- (b) Reduction of alkynes with sodium and ammonia gives trans-products (3)
- (c) Halogenation of 2-butene is stereoselective. (7)
- (d) Bimolecular elimination is both stereoselective and stereospecific (12)

QUESTION 2

- (a) Write all steps in the mechanism for any reaction which involves anchimeric assistance clearly indicating the stereochemistry of both the reactant and product with or without anchimeric assistance. (10)
- (b) Write the mechanism and names of all the products for the following reactions:
 - (i) Electrophilic addition of any hydrogen halide to 3,3-dimethyl-1-butene
 - (ii) Dehydration of 3,3-dimethyl-2-butanol in the presence of acid
 - (iii) Conversion of propanoic acid to butanoic acid (15)

QUESTION 3

- (a) Outline all steps in the following reactions:
 - (i) Conversion of 1-butanol to 2-ethyl-1-hexanol
 - (ii) Conversion of benzaldehyde to 1,3-diphenylpropenone
 - (iii) Conversion of diethyl hexanedioate (diethyl adipate) to ethyl 2-oxocyclopentane carboxylate. (15)
- (b) Outline all steps in the synthesis of 3-methyl-2-hexanone starting with ethyl acetoacetate (10)

QUESTION 4

- (a) Define the following terms and illustrate with an example in each case:
 - (i) Concerted reaction
 - (ii) Conrotatory motion (6)

- (b) Write structures of the following compounds and products of their photochemical reactions:
- (i) Cyclobutene
 - (ii) 1,3-Cyclohexadiene
 - (iii) *trans,trans*-2,4-Hexadiene
 - (iv) *trans*-5,6-Dimethyl-1,3-cyclohexadiene (9)
- (c) Write the Woodward-Hoffmann rules for electrocyclic reactions (4)
- (d) Why does ethene dimerise easily in the presence of light but it does not dimerise when it is heated? (6)

QUESTION 5

- (a) What is an aromatic compound and how can it be distinguished from an anti-aromatic compound? (5)
- (b) Outline the mechanism for the chlorination of benzene in the presence of iron (III) chloride (5)
- (c) Give reasons why nucleophilic substitution occurs readily with alkyl halides while it is difficult with aryl halides (15)

QUESTION 6

- (a) Define the following terms:
- (i) Auxochrome
 - (ii) Fingerprint region
 - (iii) Blue shift. (6)
- (b) Describe how infra red spectroscopy can be used to distinguish between the following pairs of compounds:
- (i) A carboxylic acid and an alcohol
 - (ii) A concentrated phenol and a diluted phenol
 - (iii) An amide and an amine. (6)
- (c) What is the structure of a compound, C_9H_{12} which has δ values of 7.1, 2.2, 1.5 and 0.9 ppm in the 1H NMR signals? (8)

(d) The mass spectrum of 1-(4-methylphenyl)-ethanol shows an abundant ion at m/z 121 and a less abundant ion at m/z 119. Write the structures for the two ions. (5)