UNIVERSITY OF SWAZILAND
MAIN EXAMINATION 2009/10

TITLE OF PAPER : **ADVANCED ORGANIC CHEMISTRY**

COURSE NUMBER : C403

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

(a) (i) Write the structure and name of each organic compound that may be produced when bromobenzene reacts with sodium in diethyl ether. (4)

(ii) Write the mechanism of the reaction for all the products formed in (a)(i) above. (5)

(b) Account for the following observations:

(i) The chlorination of biphenyl usually gives p-chlorobiphenyl and o-chlorobiphenyl but not m-chlorobiphenyl. (3)

(ii) When 4-chlorobiphenyl is chlorinated 4,4'-dichlorobihenyl and a little of 2,4'-dichlorobiphenyl are obtained. (5)

(c) Write equation for the reaction of bromine with each of the following compounds and show the structures and names of the products:

(i) Diphenyl methane (2)

(ii) Triphenyl methane (2)

(d) Outline how you would convert triphenylcarbinol to tetraphenylmethane (4)

QUESTION 2

(a) Write all steps in the conversion of benzene to naphthalene by Harworth synthesis. (6)

(b)(i) Outline all steps in the conversion of 2-nitronaphthalene to p-(2-naphthalene azo) phenol. (5)

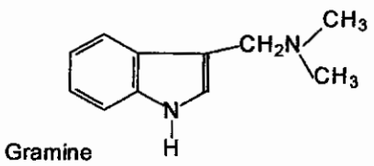
(ii) What is the use of p-(2-naphthalene azo) phenol in the industry and how is the structure of the compound related to its use? (3)

(c) Write the mechanism for the electrophilic attack of chlorine on anthracene and show how it can lead to either substitution-product or addition-product. Name the products. (7)

(d) Outline all steps in the conversion of benzene to anthracene. (4)

QUESTION 3

(a) (i) Write equation to show the conversion of indole to gramine. (3)
(ii) What is the synthetic importance of gramine? Give two examples to illustrate. (5)



Gramine

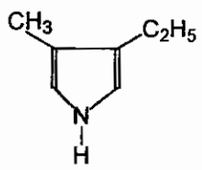
(b) Write the resonating structures of the intermediate carbocation that is produced during electrophylic substitution of indole. (4)

(c) Outline all steps in the conversion of 1,5-pentanediamine to pyridine. (6)

(d) (i) Outline steps in the conversion of 2-propenal, (acrolein) to 3-pyridine carboxylic acid, (nicotinic acid or niacin). (3)
(ii) What is the importance of niacin? (2)
(iii) What is the importance of isonicotinic acid hydrazide, (isoniazide)? (2)

QUESTION 4

(a)(i) Write all steps in the conversion of aminoacetone, $CH_3COCH_2NH_2$ and ethylacetopyruvate, $CH_3COCH_2COCO_2C_2H_5$ to opsopyrrole.

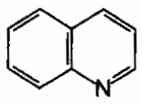


Opsopyrrole (6)

(ii) Write the IUPAC name of opsopyrrole. (1)

(b) Write the structure and name of the product of reaction of thiophene with each of the following reagents:
(i) Sulphuric acid (2)
(ii) Fuming nitric acid in acetic anhydride (2)
(iii) Acetyl chloride in presence of stannic chloride in benzene (2)
(iv) Thionyl chloride (2)

(c) Write all steps that may be involved in the Skraup synthesis of quinoline.



Quinoline

(10)

QUESTION 5

(a) Outline all steps in the synthesis of aldotetroses using the Kiliani-Fisher method starting with D-glyceraldehyde and name the aldotetroses. (11)

(b) Account for the following: Appropriate structures are essential.

(i) Although lactose, maltose and sucrose are all disaccharides, lactose and maltose are reducing sugars but sucrose is not. (6)

(ii) D-Glucose and D-mannose give the same osazone when they react with phenylhydrazine. (4)

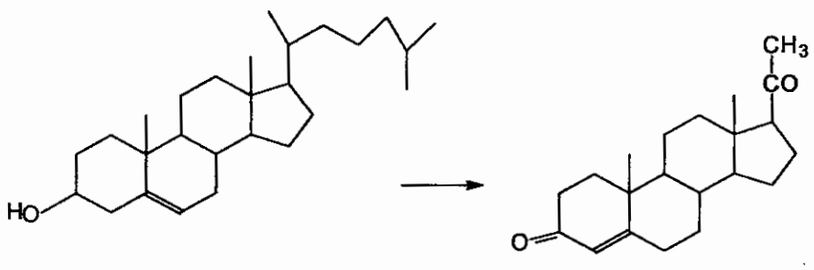
(iii) β-D-(+)-Glucopyranose is more stable than α-D-(+)-Glucopyranose. (4)

QUESTION 6

(a)(i) What is a steroid? (2)

(ii) Write briefly on the importance of steroids with appropriate examples. (4)

(b) Outline all steps in the following transformation: (11)



(c) Describe briefly how you would detect each of the following groups in an alkaloid sample:

(i) Phenolic hydroxyl (2)

(ii) Carboxyl (2)

(iii) Carbonyl (2)

(iv) Alcoholic hydroxyl (2)