2411/303
ORGANIC CHEMISTRY
Oct./ Nov. 2017
Time: 3 Hours

THE KENYA NATIONAL EXAMINATIONS COUNCIL

DIPLOMA IN ANALYTICAL CHEMISTRY

ORGANIC CHEMISTRY

3 hours

INSTRUCTIONS TO CANDIDATES

You should have the following for this examination:
Answer booklet;
Scientific calculator (Non programmable).
*This paper consists of **TWO** sections; **A** and **B**.*
*Answer **ALL** the questions in section **A** and any **THREE** questions from section **B**.*
*Each question in section **A** carries **4** marks while each question in section **B** carries **20** marks.*
Maximum marks for each part of a question are indicated.
Candidates should answer the questions in English.

This paper consists of 7 printed page.

Candidates should check the question paper to ascertain that all the pages are printed as indicated and that no questions are missing.

SECTION A (40 marks)

Answer ALL the questions in this section.

1. Calculate the heat of combustion of methane at 25° C, given the following bond energies:
C – H = 413 kJmol^{-1}; O=O = 498.3 kJmol^{-1}; C=O = 803.3 kJmol^{-1}; O—H = 462.8 kJmol^{-1}. (4 marks)

2. A compound has molecular formular $CH_3CHIC_2H_5$. Draw the following structural projections for the molecule:

   (i) Newman; (2 marks)
   (ii) Fischer. (2 marks)

3. Give structural formulas for the reactants that yield 2-butene when treated with the following reagents:

   (i) heating with concentrated H_2SO_4; (1 mark)
   (ii) alcoholic KOH; (1 mark)
   (iii) zinc dust and an alcohol; (1 mark)
   (iv) hydrogen and a catalyst. (1 mark)

4. Pentane is isomeric, on substitution of one hydrogen atom it yields a chlorine atom; it yields several alkylhalides. Identify the isomer that yields:

   (a) only a primary alkylhalide; (1 mark)
   (b) secondary halides; (2 marks)
   (c) a tertiary halide. (1 mark)

5. The following equation shows preparation of 1-bromoheptane from 1-heptanol. Write the reaction mechanism involved. (4 marks)

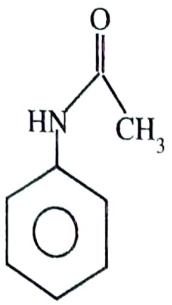
$$CH_3(CH_2)_5CH_2OH + HBr \longrightarrow CH_3(CH_2)_5CH_2Br + H_2O$$

6. For each of the following reactions, give the product and name it using IUPAC system.

   (a) $C_6H_5MgBr \xrightarrow[2.\ H_2O]{1.\ CH_3COCH_3}$; (2 marks)

   (b) $C_6H_5CHO \xrightarrow[2.\ H_2O]{1.\ (CH_3)_2CHMgCl}$. (2 marks)

7. The structure below represents acetominophen, a pain reliever produced by reacting 4-aminophenol with acetic anhydride.



Outline a synthesis scheme of acetominophen showing all steps and inorganic reagents involved. (4 marks)

8. Write a reaction mechanism for base induced hemiacetal formation with OR^- in ROH. (4 marks)

9. A tertiary alkylhalide $(CH_3)_3$ CBr undergoes S_N1 hydrolysis. Write the mechanism for the steps involved during the hydrolysis. (4 marks)

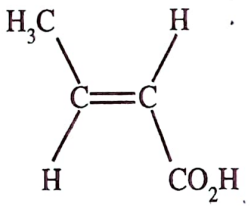
10. Write an equation showing hydroboration - oxidation of 1-methylcyclohexene. Name the product formed systematically. (4 marks)

SECTION B (60 marks)

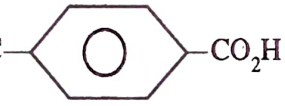
*Answer **THREE** questions from this section.*

11. (a) Give IUPAC names for each of the following carboxylic acids:

(i) $H_2C{=}C(CO_2H)CH_3$ (1 mark)

(ii)  (1 mark)

(iii) $HO_2C\,CO_2H$ (1 mark)

(iv)  (1 mark)

(b) (i) Write the common names of the carboxylic acids in (a)(i) and (a)(iii) above.

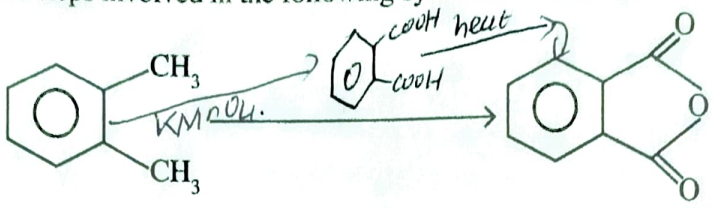
(2 marks)

(ii) State **one** industrial application of the carboxylic acid in (a)(i) above.

(1 mark)

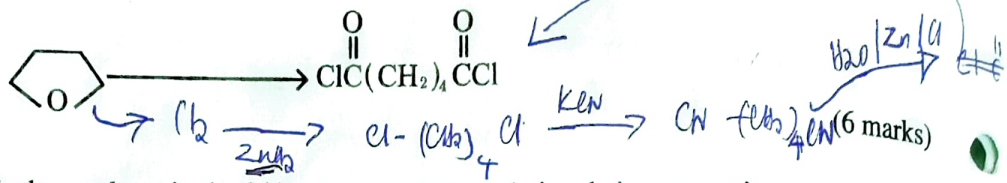
(c) Show the steps involved in the following synthetic transformations:

(i)



(3 marks)

(ii)



(6 marks)

(d) Identify the products in the following reactions and give their systematic names:

(i) $COCl_2 + NH_3 \longrightarrow$

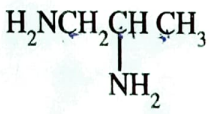
(2 marks)

(ii) $COCl_2 + C_2H_5OH \longrightarrow$

(2 marks)

12. (a) Name the following amines.

(i)

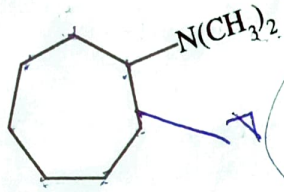


(1 mark)

(ii)

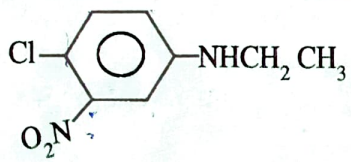
(1 mark)

(iii)



(1 mark)

(iv)

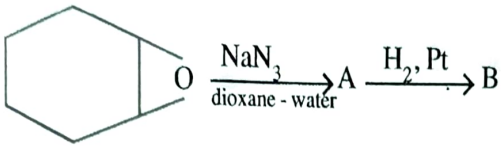


(1 mark)

(b) Using a resonance structure, explain why ortho-cyanoaniline is a weaker base than aniline. (6 marks)

(c) Starting with butylbromide, show how butylamine can be synthesized via Gabriel synthesis method. Name all the intermediates formed. (6 marks)

(d) Complete the following reaction by identifying the products A and B. Give their systematic names. (4 marks)



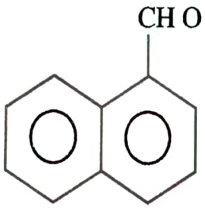
13. (a) Explain why nitrobenzene is used as a solvent for Freidel-Crafts alkylation of bromobenzene and not benzene. (4 marks)

(b) Using appropriate inorganic and organic reagents show how the following compounds can be synthesised from benzene. Show all the steps involved.

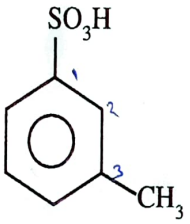
(i) ortho-chlorotoluene; (7 marks)

(ii) 1,3-dimethyl-2-ethylbenzene. (7 marks)

(c) Name the following compounds systematically:

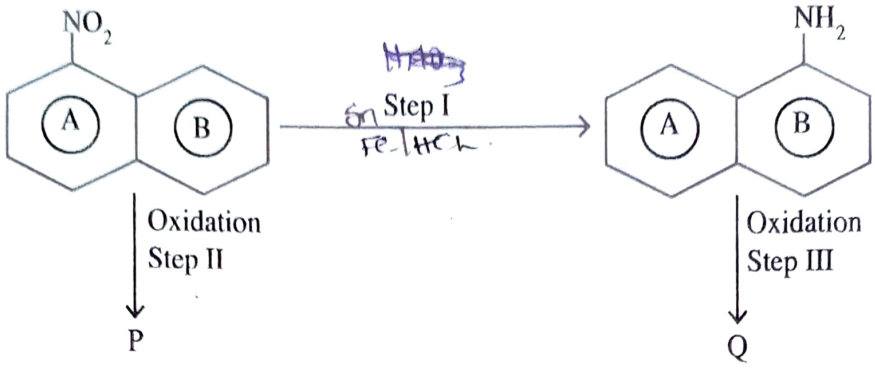
(i) 

Naphthalene aldehyde (1 mark)

(ii) 

Toluene Sulphonic acid (1 mark)

14. (a) Study the following reaction scheme and answer the questions that follow.



(i) Identify the reagents used in step I. (2 marks)

(ii) Give the structures and names of products P and Q. (4 marks)

(iii) Explain how product P is formed. (2 marks)

(b) Write the structures of the following compounds:

(i) 2-benzoylthiophene; (1 mark)

(ii) 3-furansulfonic acid; (1 mark)

(iii) 2,3-dichloropyrrole. (1 mark)

(c) Show the steps and reagents involved in the synthesis of the following compounds from 3-picoline (3-methlypyridine):

(i) 3-pyridine carboxylic acid; (3 marks)

(ii) 3-pyridine carboxylic acid hydroazide. (6 marks)

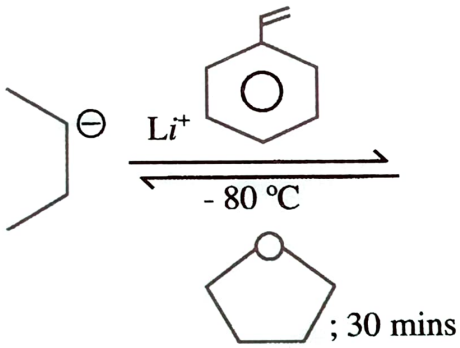
15. (a) List the **three** mechanistic steps involved in uncontrolled chain-growth polymerization. (3 marks)

(b) For the sequential anionic block coplymerizations of styrene and α-methyl styrene under the given conditions, show the:

(i) electron arrow-pushing mechanism; (6 marks)

(ii) intermediates; (4 marks)

(iii) final products. (4 marks)



(c) Benzylperoxide is used in polymerization of ethene. Using an equation, explain the role of benzylperoxide in this process. (3 marks)