



MACHAKOS UNIVERSITY

University Examinations for 2021/2022 Academic Year

SCHOOL OF PURE AND APPLIED SCIENCES

DEPARTMENT OF PHYSICAL SCIENCES

THIRD YEAR SECOND SEMESTER EXAMINATION FOR

BACHELOR OF EDUCATION (SCIENCE)

BACHELOR OF EDUCATION (SPECIAL NEEDS EDUCATION)

BACHELOR OF SCIENCE IN ANALYTICAL CHEMISTRY

SCH 302: THE CHEMISTRY OF AROMATIC COMPOUNDS

DATE:

TIME:

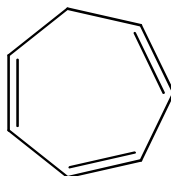
INSTRUCTIONS:

- The paper consists of **two** sections.
- Section **A** is **compulsory** (30 marks).
- Answer any **two** questions from section **B** (each 20 marks).

SECTION A (COMPULSORY)

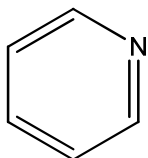
QUESTION ONE (30 MARKS)

- a) Menthol, an analgesic used in many ointments for the relief of pain, releases a peppermint aroma upon exposure to air. Based on this observation, discuss whether this implies that it has a benzene ring in its chemical structure. (2 marks)
- b) The electron cloud of benzene is said to be below and above the ring. With illustration, justify this observation. (4 marks)
- c) In the presence of UV light, chlorine substitutes into the methyl group of methylbenzene, and not into the ring. What conditions are necessary for ring substitution? (2 marks)
- d) Removal of hydride (H^-) or a proton from cycloheptatriene below gives an anion or cation. Which process is more likely? Sketch the pi MO diagrams for both species as part of your answer. (7 marks)

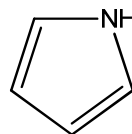


cyclohepta-1,3,5-triene

- e) Both pyridine and pyrrole (shown below) are aromatic molecules. How do you account for the fact that pyrrole is less basic than pyridine. (4 marks)

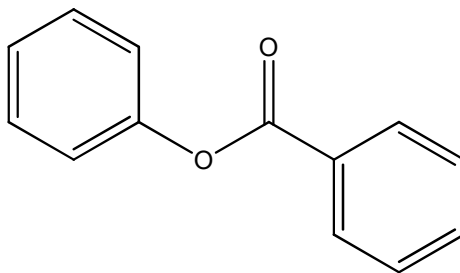


pyridine



pyrrole

- f) With proper justification, determine if the statements below are true or false. (4 marks)
- Statement I: Furan is an aromatic ring system, has resonance energy comparable to that of benzene
- Statement II: Furan decolourises the brown colour of bromine water solution.
- g) One ring of phenyl benzoate undergoes electrophilic aromatic substitution much more readily than the other. Identify which one it is and explain your answer. (2 marks)

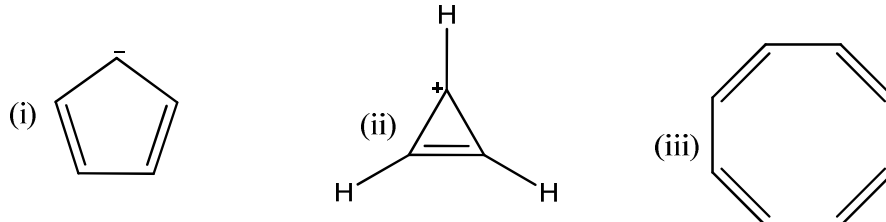


- h) You are required to synthesize Pentylbenzene in the laboratory. Starting with benzene and any other reagent, provide the appropriate pathway for its synthesis. (5 marks)

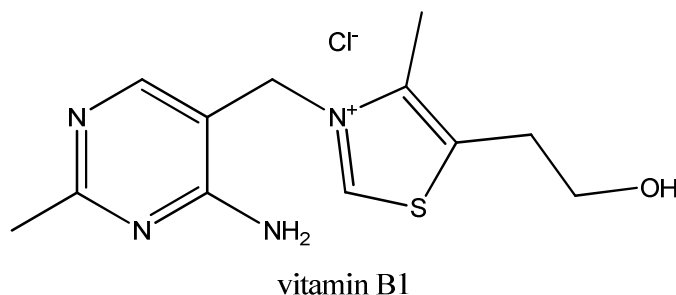
SECTION B (ANSWER ANY TWO QUESTIONS)

QUESTION TWO (20 MARKS)

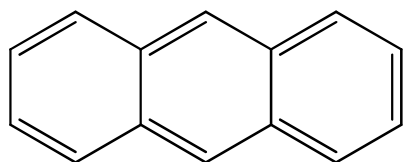
- a) Use resonance theory to explain why the hydroxyl of phenol is an activating group and an ortho para director. Illustrate your explanation by showing the carbocation intermediates formed when phenol reacts with a Br^+ ion at the ortho, meta and para position. (6 marks)
- b) Using the polygon rule (Frost circles), predict the molecular orbital diagram for the following species and determine whether they are aromatic or not. (6 marks)



- c) Thiamin, or vitamin B1, contains a positively charged five-membered nitrogen–sulfur heterocycle called a thiazolium ring. With reasons, determine whether thiazolium ring is aromatic. (2 marks)



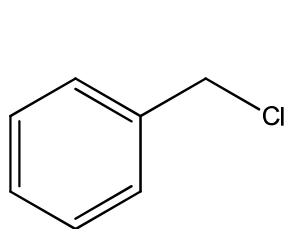
- d) Electrophilic substitution of toluene is much faster in comparison to benzene. For example, sulfonation of benzene takes 20 to 30 min to complete while that of toluene takes one minute only. Discuss the basis of their different reactivities. (3 marks)
- e) Draw all the resonance structures for anthracene shown below. (3 marks)



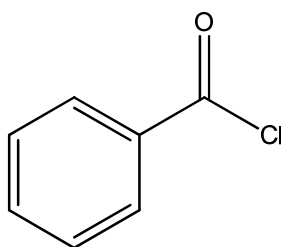
Anthracene

QUESTION THREE (20 MARKS)

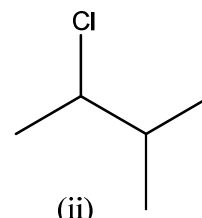
- a) Following the relevant mechanism, explain why electrophilic substitution in naphthalene occurs mostly at the α -position. (3 marks)
- b) Provide the mechanism and structural formula for the product formed by Friedel–Crafts alkylation or acylation of benzene with the following: (9 marks)



(i)



(ii)

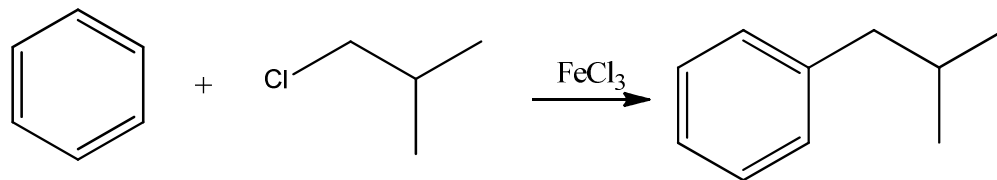


(ii)

- c) Chlorine is an electron withdrawing group and naturally it is supposed to be a meta-director. However, it is an ortho-para director. Explain by drawing resonance structures of carbocation intermediates in ortho, meta, and para electrophilic substitution reaction of chlorobenzene using Electrophile E^+ . (6 marks).
- d) Nitrobenzene does not undergo Friedel–Crafts alkylation. Explain. (2 marks)

QUESTION FOUR (20 MARKS)

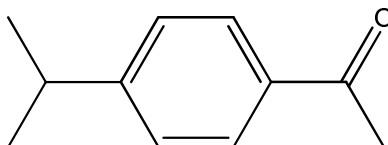
- a) The following alkylation reaction doesn't yield the compound shown as the major product. Predict the major product and provide a mechanism for the reaction. (6 marks)



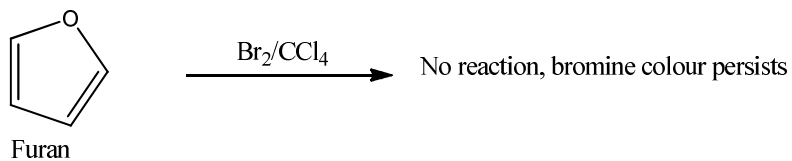
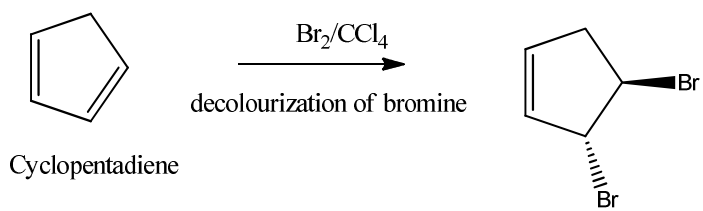
- b) 2,6-Di-*tert*-butyl-4-methylphenol, more commonly known as butylated hydroxytoluene, or BHT, is used as an antioxidant. BHT is synthesized industrially from 4-methyl phenol by reaction with 2-methylpropene in the presence of sulphuric acid. Propose a mechanism for this reaction. (6 marks)
- c) Discuss why benzene reactions differ from those of other conjugated systems (4 marks).
- d) The methyl group in methyl benzene is 2,4-directing. Explain what this means using nitration as an example. (4 marks)

QUESTION FIVE (20 MARKS)

- a) The following ketone is isolated from the roots of several members of the iris family and is used as fragrance in perfumes. Describe the synthesis of this ketone from benzene. (6 marks)



- b) The methyl group in methylbenzene is 2, 4-directing (ortho, para-directing). Draw the resonance structures of the carbocation intermediates formed by ortho, meta, para electrophilic attack. Use these resonance structures to account for the primary observation of formation of only two products substituted at ortho and para positions. (4 marks)
- c) Both cyclopentadiene and furan have two double bonds, however when both are subjected to bromination in carbon tetrachloride they react differently as shown below. Explain this observation. (4 marks)



- e) Using resonance structures of the intermediates, explain why bromination of biphenyl occurs at ortho and para positions rather than meta. (6 marks)

