



MACHAKOS UNIVERSITY

University Examinations 2021/2022

SCHOOL OF PURE AND APPLIED SCIENCES

DEPARTMENT OF PHYSICAL SCIENCES

THIRD YEAR SECOND SEMESTER EXAMINATION FOR
BACHELOR OF EDUCATION (SPECIAL NEEDS EDUCATION)

BACHELOR OF SCIENCE (ANALYTICAL CHEMISTRY)

BACHELOR OF EDUCATION (SCIENCE)

SCH 302: THE CHEMISTRY OF AROMATIC COMPOUNDS

DATE: xx/12/2022

TIME: 2 Hrs

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) Discuss the limitations of Kekulé description of benzene structure. (4 marks)
- b) 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. (4 marks)
- (i) Aromaticity
 - (ii) Electrophilic aromatic substitution
 - (iii) Lewis acid
 - (iv) Spectroscopy

d) Draw the structures corresponding to the following names: (5 marks)

(i) 4-iodo-1,2-dimethylbenzene

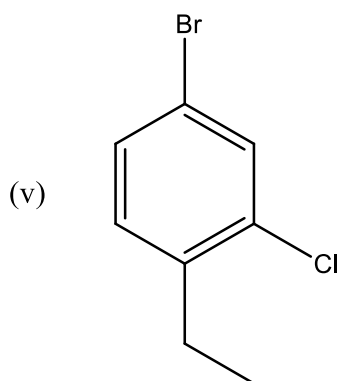
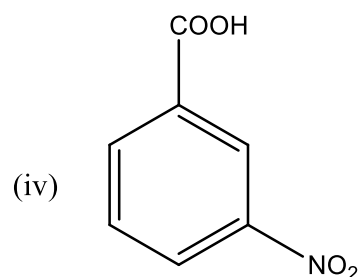
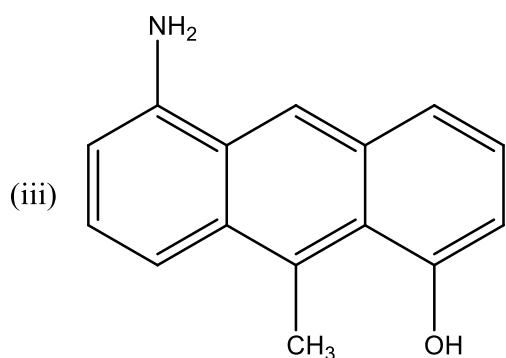
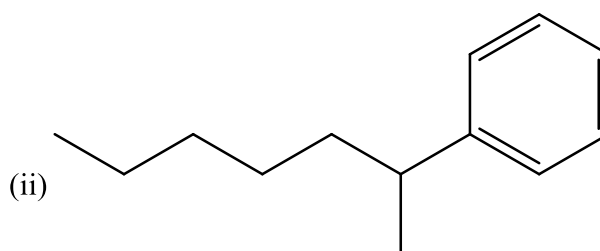
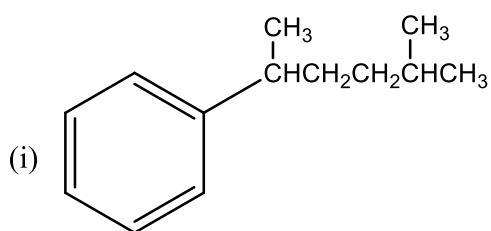
(ii) 2,4-dichlorophenol

(iii) 1-Cyclohexyl-3-ethylbenzene

(iv) 1-Phenylcyclopropanol

(v) Tertbutyl benzene

e) Provide the IUPAC names of the following benzene derivatives (5 marks)



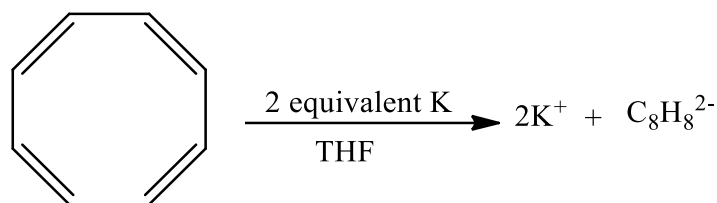
- f) Using heats of hydrogenation, discuss the observed stability of benzene. (6 marks)
- g) The electron cloud of benzene is said to be below and above the ring. With illustration, justify this observation. (4 marks)

SECTION B (ANSWER ANY TWO QUESTIONS)

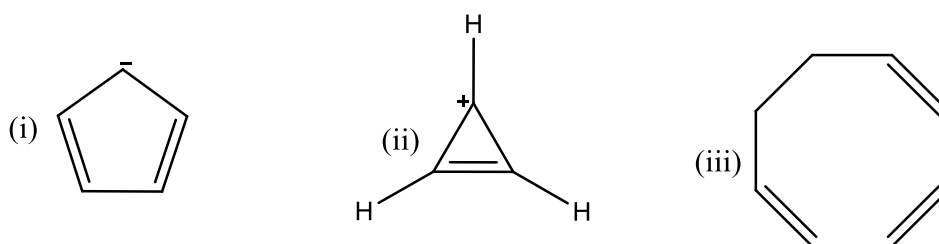
QUESTION TWO (20 MARKS)

- a) In 1960 T. Katz (Columbia University) showed that cyclooctatetraene adds two electrons when treated with potassium metal to form a stable, planar dianion, $C_8H_8^{2-}$ (as the dipotassium salt). Draw the structure of $C_8H_8^{2-}$ and explain why it is stable.

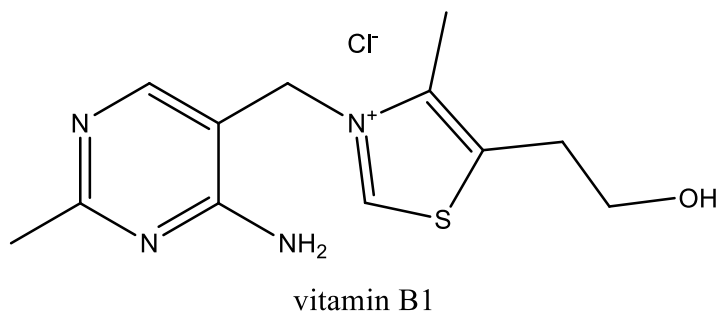
(4 marks)



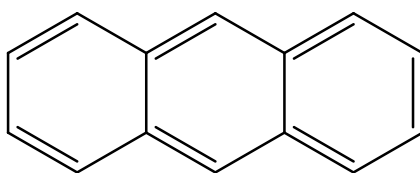
- b) Using the polygon rule (Frost circles), predict the molecular orbital diagram for the following species and determine whether they are aromatic or not. (4 marks)



- 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)

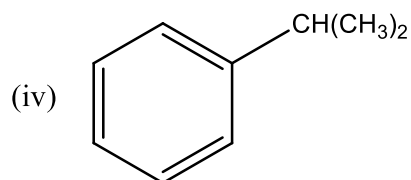
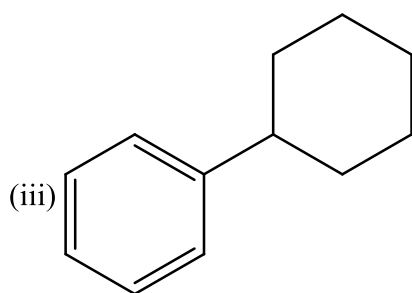
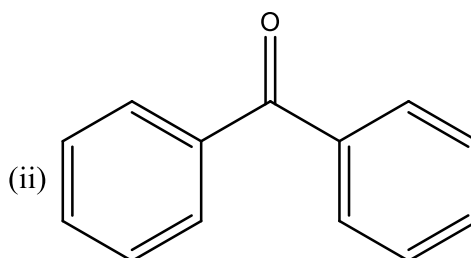
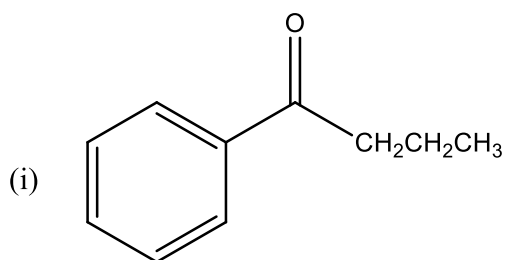


- d) Draw all the resonance structures for naphthalene shown below. (3 marks)



anthracene

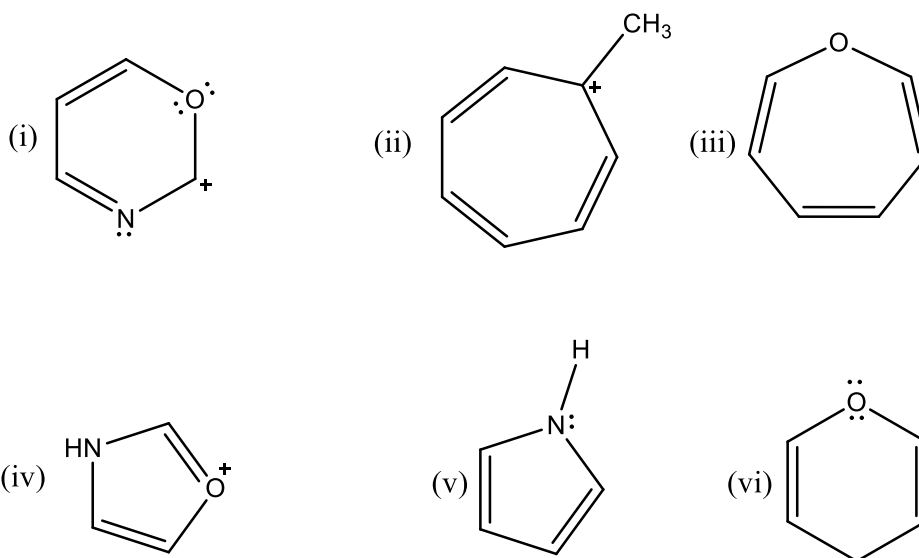
- e) Identify the acid halides and alkyl halides necessary to produce Friedel-Crafts acylation and alkylation products shown below. (4 marks)



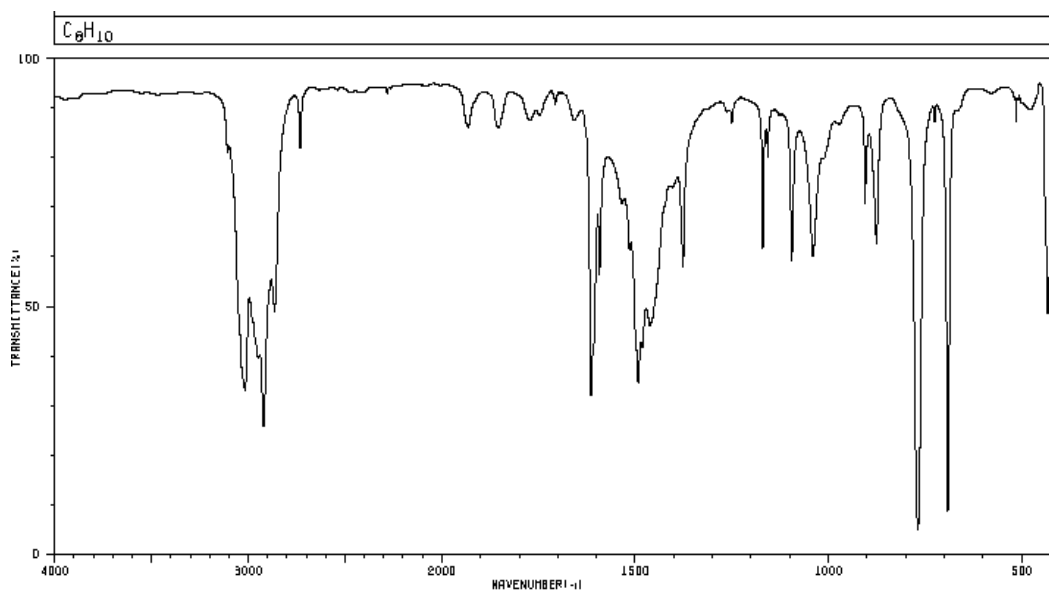
- f) Friedel-Crafts alkylation reactions are prone to rearrangement. Starting with benzene and propylchloride demonstrate how rearrangement takes place. (3 marks)

QUESTION THREE (20 MARKS)

- a) With reasons, classify the following compounds as either aromatic, anti-aromatic or non-aromatic. (6 marks)



- b) The substitution reaction of toluene with Br_2 can, in principle, lead to the formation of three isomeric bromotoluene products. In practice, however, only o- and p-bromotoluene are formed in substantial amounts. The meta isomer is not formed. Draw the structures of the three possible carbocation intermediates and explain why ortho and para products predominate over meta (4 marks)
- c) The diagram shown below is an IR spectra of one of the xylenes. Identify the xylene and provide reasons for assigning the particular xylene to the spectra. (2 marks)



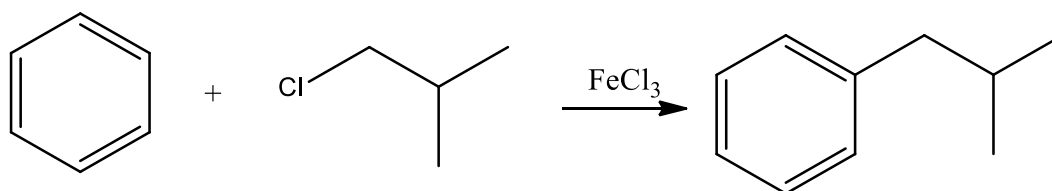
d) Discuss the basis of Hückel's rule using Molecular Orbital (MO) Theory. (6 marks)

e) Cyclobutadiene undergoes Diels-Alder reaction to form a Diels-Alder product. Discuss why this is so and show the product formed following the appropriate mechanism. (2 marks)

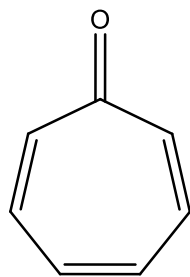
QUESTION FOUR (20 MARKS)

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.

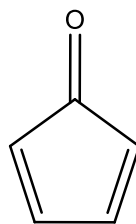
(6 marks)



b) Cyclohepta-2,4,6-trienone is stable, but cyclopenta-2,4-dienone is so reactive that it can't be isolated. Propose an explanation for the different stabilities taking the polarity of the carbonyl group into account. (4 marks)



cyclohepta-2,4,6-trienone

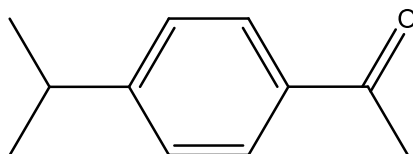


cyclopenta-2,4-dienone

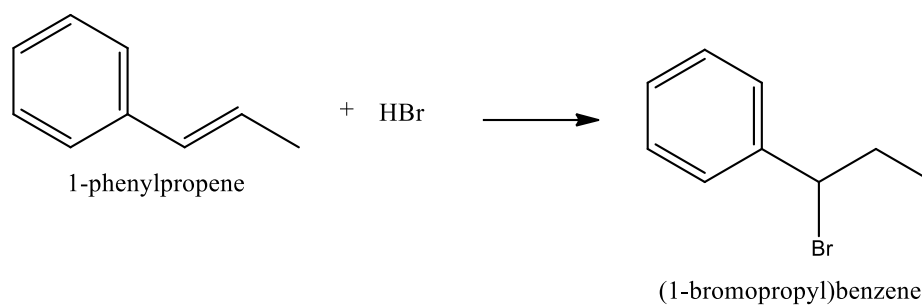
- c) 2,6-Di-*tert*-butyl-4-methylphenol, more commonly known as butylated hydroxytoluene, or BHT, is used as an antioxidant. BHT is synthesized industrially from 4-methyl phenol by reaction with 2-methylpropene in the presence of sulphuric acid. Propose a mechanism for this reaction. (6 marks)
- d) Discuss the criteria for aromaticity. (4 marks)

QUESTION FIVE (20 MARKS)

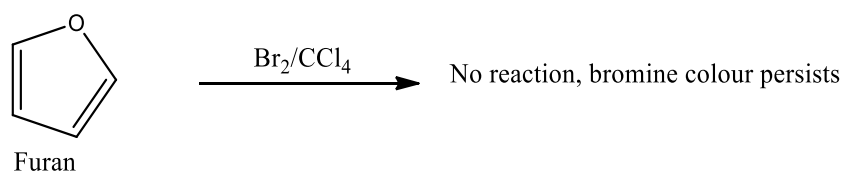
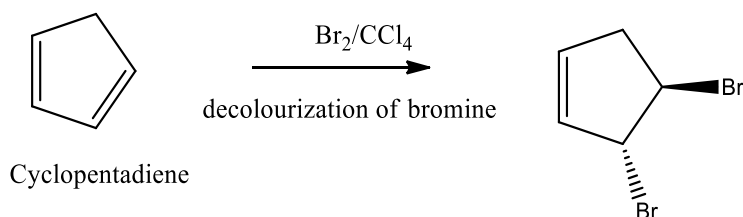
- a) The following ketone is isolated from the roots of several members of the iris family and is used as fragrance in perfumes. Describe the synthesis of this ketone from benzene. (6 marks)



- 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) Addition of HBr to 1-phenylpropene yields only (1-bromopropyl) benzene. Propose a mechanism for the reaction, and explain why none of the other regioisomer is produced. (3 marks)



- d) 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) Imidazole (shown below) has two nitrogens, where N3 is relatively basic (like the nitrogen of pyridine), while N1 is relatively nonbasic (like the nitrogen of pyrrole). Explain the different basicities of these two nitrogens. (3 marks)

