MACHAKOS UNIVERSITY

University Examinations 2021/2022

SCHOOL OF PURE AND APPLIED SCIENCES

DEPARTMENT OF PHYSICAL SCIENCES

THIRD YEAR SUPPLEMENTARY/SPECIAL 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: 16/03/2022 **TIME: 2:00-4:00PM**

INSTRUCTIONS:

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

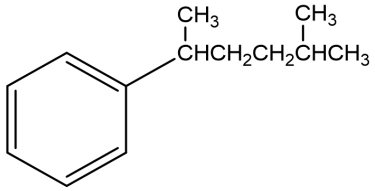
SECTION A (COMPULSORY)

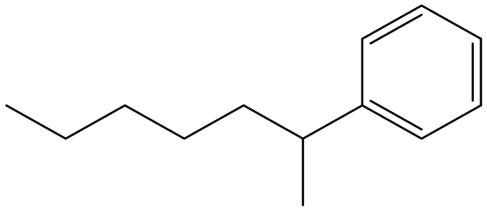
QUESTION ONE (30 MARKS)

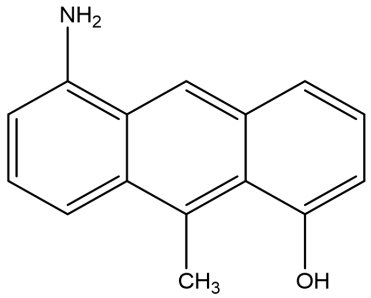
a) Draw the structures corresponding to the following names (5 marks)

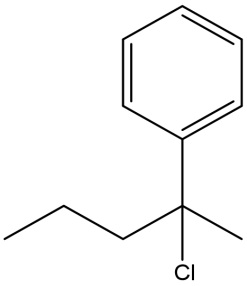
(i) *p*-Bromochlorobenzene
(ii) *p*-Bromotoluene
(iii) Methylbenzene sulfonic acid
(iv) 1-Chloro-3,5-dimethylbenzene
(v) Isobutyl benzene

b) Provide the IUPAC names of the following compounds (4 marks)

(i) 

(ii) 

(iii) 

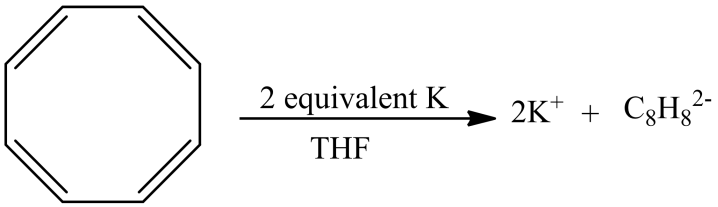
(iv) 

c) Attempts to come up with the structure of benzene started in the early 19th century. One of the first people to attempt was August Kekulé. Describe the Kekulé proposal on the structure of benzene and give reasons why it was latter disapproved. (6 marks)

d) The electron cloud of benzene is said to be below and above the ring. With illustration, justify this observation. (4 marks)

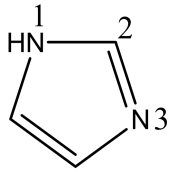
e) In 1960 T. Katz (Columbia University) showed that cyclooctatetraene adds two electrons when treated with potassium metal and forms a stable, planar dianion, $C_8H_8^{2-}$ (as the dipotassium salt). Use the molecular orbital diagram to explain this result.

(4 marks)



f) Discuss two main sources of aromatic hydrocarbons. (4 marks)

g) 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)



imidazole

PART B (ANSWER ANY TWO QUESTIONS)

QUESTION TWO

a) Molecules are said to be aromatic if they satisfy a number of requirements.

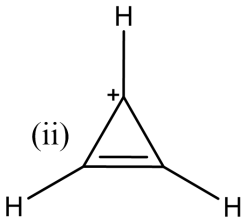
(i) Discuss these requirements (4 marks)

(ii) Using the Molecular orbital diagram for benzene justify one of the requirements mentioned in (i). (6 marks)

b) Using the polygon rule (polygon and circle method), determine whether the following species are aromatic. (4 marks)

(i)

(ii)



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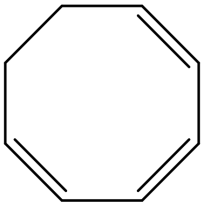
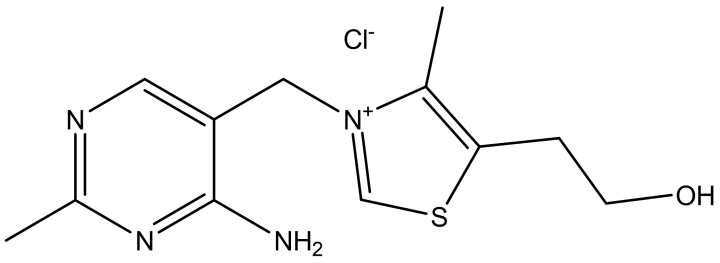


c) Thiamin, or vitamin B1, contains a positively charged five-membered nitrogen–sulfur heterocycle called a thiazolium ring. With reasons, determine whether thiazolium ring is aromatic. (2 marks)

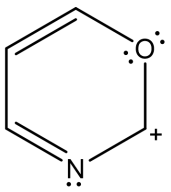


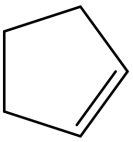
vitamin B1

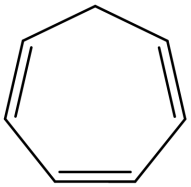
d) Following the correct mechanism, provide the product formed in alkylation of benzene using I-chlorobutane. (4 marks)

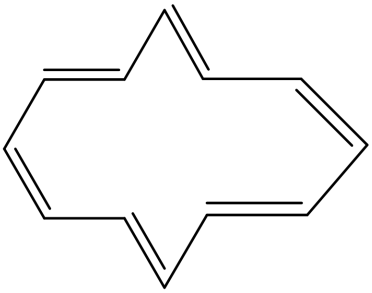
QUESTION THREE

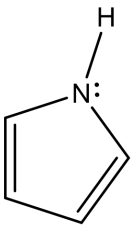
a) Providing reasons, classify the following compounds as either aromatic, anti-aromatic or non-aromatic. (6 marks)

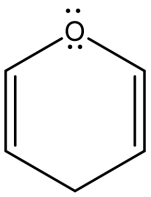
(i) 

(ii) 

(iii) 

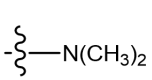
(iv) 

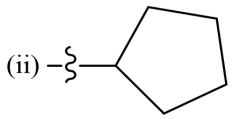
(v) 

(vi) 

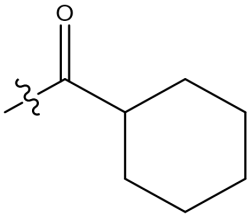
b) The substitution reaction of toluene with Br_2 can, in principle, lead to the formation of ree isomeric bromotoluene products. In practice, however, only o- and p-bromotoluene are formed in substantial amounts. The meta isomer is not formed. Draw the structures of the three possible carbocation intermediates and explain why ortho and para products predominate over meta
(4 marks)

c) Identify each of the following groups as an activator or deactivator and as an o,p-director or m-director (4 marks)

(i) 

(ii) 

(iii) 

(iv) 

d) Draw all the resonance structures of cyclopentadienyl anion and determine whether it is aromatic, antiaromatic or non-aromatic using Molecular Orbital (MO) Theory.

(4 marks)

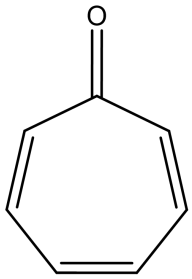
e) Cyclobutadiene undergoes Diels-Alder reaction to form a Diels-Alder product. Discuss why this is so and show the product formed following the appropriate mechanism.

(2 marks)

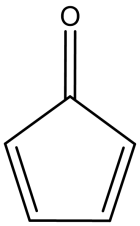
QUESTION FOUR

a) Benzene is said to be highly stable compared to other unsaturated compounds. Confirm this statement using heats of hydrogenation. (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)

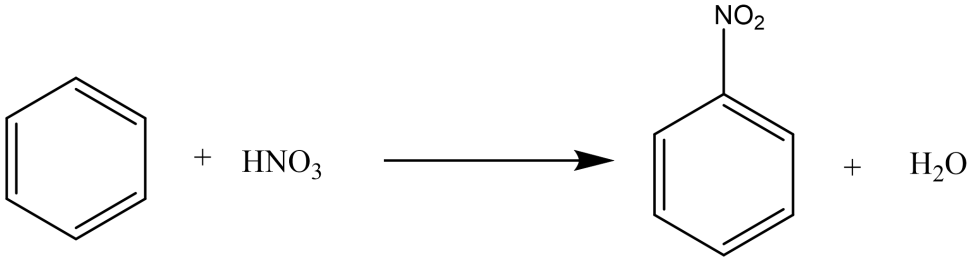


cyclohepta-2,4,6-trienone



cyclopenta-2,4-dienone

c) Nitration of benzene involves the reaction between benzene and concentrated nitric acid: as shown below.



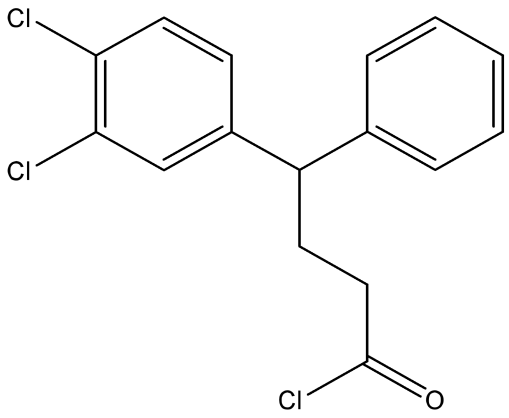
(i) State the conditions for the reaction.
(ii) The electrophile in this case is the nitronium ion, NO_2^+. Write an equation showing its formation.
(iii) Give the mechanism for the reaction. (6 marks)

d) The carbocation electrophile in a Friedel–Crafts reaction can be generated in ways other than by reaction of an alkyl chloride with $AlCl_3$. For example, reaction of benzene with 2-methylpropene in the presence of H_3PO_4 yields a Friedel-craft

alkylation. Propose a mechanism for this reaction and provide the product name
(4 marks)

QUESTION FIVE

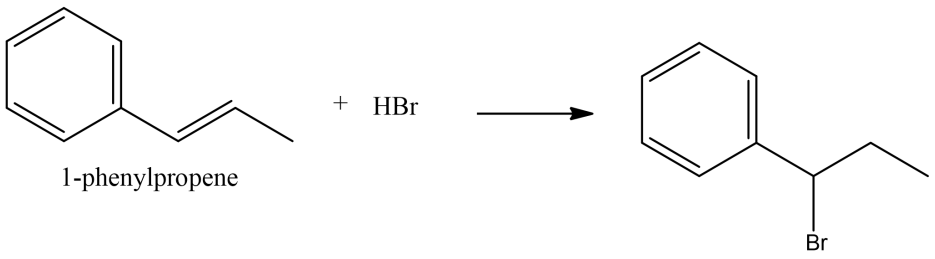
a) Show a stepwise mechanism for the intramolecular Friedel-Crafts acylation of the molecule shown below using $AlCl_3$ catalyst. (6 marks)



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 otho 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

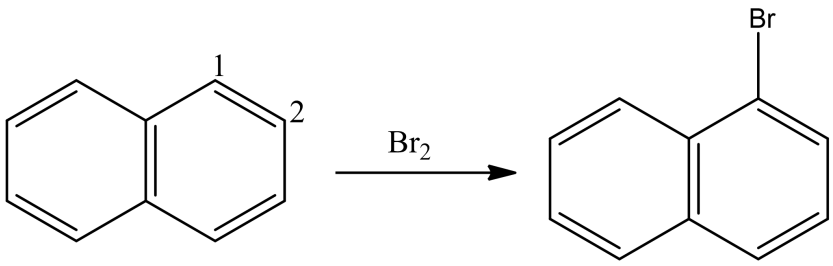
(3 marks).



1-phenylpropene

(1-bromopropyl)benzene

d) Draw resonance structures of the intermediate carbocations in the bromination of naphthalene, and account for the fact that naphthalene undergoes electrophilic substitution at C1 rather than C2 (4 marks)



e) Explain why Friedel–Crafts alkylations often give polysubstitution but Friedel–Crafts acylations do not. (3 marks)