<u>UNIVERSITY OF RUHUNA</u> BACHELOR OF SCIENCE (GENERAL) DEGREE LEVEL I – (SEMESTER I) EXAMINATIONS -- DECEMBER 2020

SUBJECT: Chemistry

COURSE UNIT: CHE 1122 (Fundamentals in organic chemistry) TIME: Two (02) hours

Answer four (04) questions only by selecting at least one (01) question form section A, B and C

Section - A

01. Answer all Parts

- (a) Use the concept of hybridization to answer the questions given below;
 - (i) Using the diagram of orbital hybridization of Carbon, explain how many sigma and π bonds are possible in the molecule of ethene.
 - (ii) Comment on the geometry of ethene based on above (i).
 - (iii) Why Boron trifluoride acts as Lewis acid in organic reactions?

(b) Use the theory of resonance to answer the questions given below;

- (i) Draw the resonance structures of formamide anion (HCONH)
- (ii) Out of the structures drawn, which one is more stable?
- (iii) Give reasoning for the answer above (ii).
- (c) Name the compounds given below using IUPAC nomenclature





(d) Draw the structures of following molecules.

- (i) 5,6-dimethyl-4-oxo-heptanal
- (ii) N,N-diethylpropanamide

02. Answer all parts

- (a) Consider ethane molecule to answer the following questions.
 - (i) Draw the eclipsed and staggered conformations of ethane using Newman Projections.
 - (ii) Name types of strain if available in each conformation drawn above.
 - (iii) What is the most stable conformation out of above two?
 - (iv) Are two conformations separable at the room temperature? Explain your answer.

(30 marks)

(30 marks)

(30 marks)

(20 marks)

(20 marks)

(b) Consider two isomers of a dicarboxylic acids given below.



- (i) Out of two acids given above, which one has the highest melting point? Explain your answer.
- (ii) When above two compounds are heated separately, an anhydride is formed. Draw the structure of anhydride.
- (iii) Which compound given above forms the anhydride rapidly? Explain your answer.

(30 marks)

(c) Assign the configuration of double bonds (i - v) of the following compound into E/Z. Give reasons for the assigning.



(20 marks)

(d) Assign the chiral center(s) of following molecules to the configuration of \mathbf{R}/\mathbf{S} .





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(20 marks)

Section – B

03. Answer all parts

(a) Giving an example briefly explain the structure of carbocation.

(15 marks)

(b) Giving reasons arrange the following carbocations **A**, **B** and **C** in the order of increasing their stability.



(15 marks)

(c) Consider the reaction given below

- (i) Predict the possible products of the above reaction.
- (ii) Give the intermediate for each of the above products proposed.
- (iii) Giving reasons identify the major product of this reaction.

(30 marks)

(d) Predict the major product of the following reactions



(iv)

H-C=C-H $1.NaNH_2$ 2. CH₃CH₂CH₂Br

(40 marks)

04. Answer all parts

- (a) Write down the product(s) of the following reactions. The type of the each reaction is given within brackets.
 - (i) $H_3C Br + CH_3CH_2O^{-}Na^{+} (E2) H_3C^{-}$
 - (ii) H_3C C-Br + CH_3OH (S_N1) H_3CH_2C (iii) H_3C H_3C

(30 marks)

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(b) Explain why methanol is more acidic (pKa=15.5) than tert-butyl alcohol (pKa=19.0).

(20 marks)

(c) Consider the following reaction scheme to synthesize **E** from **A**.



- (i) Identify the missing reagents P and Q and draw the structures of missing intermediate C and product E.
- (ii) Give a plausible mechanism for the formation of **B** from **A** by proposed reagent **P** in above (i).

(50 marks)

Section - C

05. Answer all parts

(a) Based on the structures given below answer the following questions



cyclopropene

cyclopenta-1,3-diene

- (i) State the Huckel's criteria for aromaticity.
- Using the Huckel's criteria, determine the aromaticity of the two anions.
 (cyclopropenyl anion and cyclopenta-1,3-dienyl anion) produced from the two molecules shown above.
- (iii) With reasons identify the stronger acid from these two molecules.

(30 marks)

(b) Pyridine, a nitrogen-containing heterocycle, undergoes typical aromatic substitution reactions rather than addition reactions.



- (i) Discuss the contribution of nitrogen (N) atom to the aromaticity of pyridine.
- (ii) Using polygon method deduce the aromaticity of pyridine.

(30 marks)

(c) Using the reaction scheme given below answer the questions



- (i) Show the generation of electrophile.
- (ii) Write down a plausible mechanism for the formation of major product.
- (iii) Write down an alternative method to obtain propylbenzene as the only product via aromatic acylation.

(40 marks)

06. Answer all parts

A student has proposed two synthetic routes for the synthesis of p-nitrotoluene. (a)



- With reasons choose the correct route to synthesize p-nitrotoluene. (i)
- Show the detailed mechanism for the selected route. (ii)

(25 marks)

Propose the structures for the compounds A-G in the given synthesis of phenyl benzoate. (b)



⁽²⁵ marks)

Benzene derivatives containing halogens can undergo nucleophilic aromatic substitution (c) reactions in the presence of strong base via a benzyne intermediate.



- Show the formation of the benzyne intermediate for the above reaction. (i)
- Draw the structure(s) of possible product(s) obtained from the reaction and comment (ii) on the products.

(20 marks)

(d) Giving necessary reagents, reaction conditions and intermediates formed, show how you would carry out the following conversions.



(iii)



(30 marks)