

DEPARTMENT OF CHEMISTRY
SCHOOL OF CHEMICAL AND LIFESCIENCES, JAMIA HAMDARD
MSc. CHEMISTRY, SEMESTER-II EXAMINATIONS-2022
PAPER CODE: MCHCC-202
PAPER TITLE: ORGANIC CHEMISTRY-II

(Write your Roll No. at the top immediately on receipt of this question paper)

Time: 3 hours

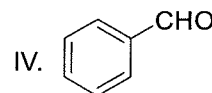
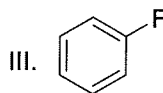
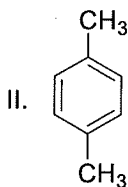
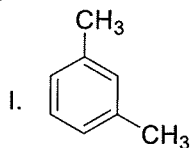
Maximum Marks: 75

Attempt all questions. All parts of a question must be attempted in continuation. Start answer of a fresh question on a new page. Cite examples and draw labelled diagrams whenever necessary.

Q1. Attempt all questions:

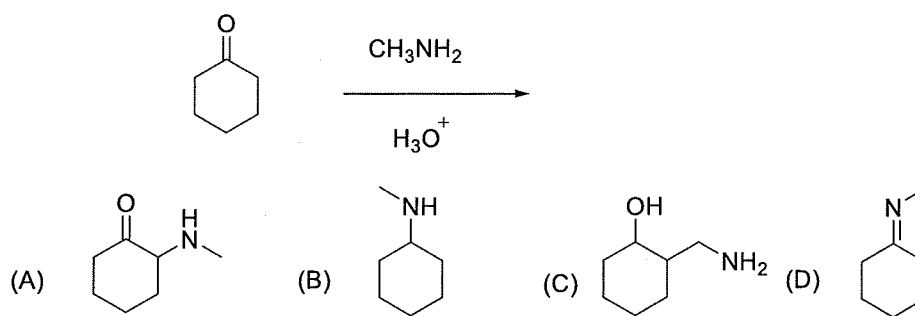
(1x15=15)

- a. Which of the following is the rate determining step in electrophilic substitution reaction?
(A) Generation of electrophile (B) Attack by an electrophilic reagent on benzene ring
(C) Formation of product (D) All of the above
- b. What is the correct increasing order of reactivity of the following compounds towards electrophilic aromatic substitution reaction?



- (A) I < II < III < IV (B) IV < III < II < I (C) IV < III < I < II (D) III < IV < I < II
- c. Which of the following is not a product of the reaction of benzene with CH_3Cl and AlCl_3 ?
(A) Toulene (B) Isopropyl benzene (C) o-Xylene (D) p-Xylene
- d. Identify the correct order of reactivity of following towards aromatic electrophilic substitution reaction.
I. Toulene II. Benzene III. Chlorobenzene IV. Nitrobenzene
(A) IV < III < II < I (B) IV < II < I < III
(C) IV < III < I < II (D) IV < I < III < II
- e. Which of the following is the major product when 2-methyl propane reacts with bromine in presence of light?
(A) 1-bromo-2-methylpropane (B) 2-bromo-2-methylpropane
(C) Both formed in equal ratio (D) None of the above
- f. How many mono halogenated products are likely to be formed when butane reacts with bromine in presence of light?
(A) 2 (B) 3 (C) 4 (D) None
- g. The reaction of 2-methyl-1-propane with HCl in the presence of H_2O_2 gives:
(A) 2-Chloro-2-methylpropane as the major product
(B) 1-Chloro-2-methylpropane as the major product
(C) No product will be formed (D) None

- h. All of the following are characteristics of a Wittig reaction except:
 (A) it proceeds through a phosphaoxetane intermediate
 (B) it results in the formation of a carbon-carbon double bond
 (C) it results in the formation of trans double bonds
 (D) it involves the reaction of a phosphonium ylide with a carbonyl
- i. What type of reaction takes place upon treatment of a ketone with HCN to form a cyanohydrin?
 (A) Nucleophilic addition (B) Nucleophilic substitution
 (C) Electrophilic addition (D) Electrophilic substitution
- j. In which condensation an enol or an enolate ion reacts with a carbonyl compound to form a β -hydroxylaldehyde or β -hydroxyketone, followed by dehydration to give a conjugated enone happens?
 (A) Aldol condensation (B) Claisen reduction
 (C) Henry condensation (D) Knoevenagel condensation
- k. What is the major organic product obtained from the following reaction?

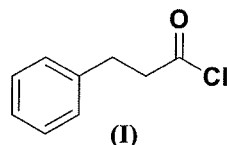


- l. Which of the following statement regarding the E2 mechanism is wrong?
 (A) Reactions by the E2 mechanism are always bimolecular
 (B) Reactions by the E2 mechanism are generally second order
 (C) Reactions by the E2 mechanism usually occur in one step
 (D) Reactions by the E2 mechanism usually occur in two steps
- m. Which of the following reacts by the E1 mechanism in ethanol most readily?
 (A) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Br}$ (B) $(\text{CH}_3)_2\text{CHCH}_2\text{CH}_2\text{Br}$
 (C) $(\text{CH}_3)_3\text{CBr}$ (D) $\text{CH}_3\text{CH}_2\text{CH}(\text{Br})\text{CH}_3$
- n. Which of the following statement regarding regioselectivity of elimination reactions is wrong:
 (A) More substituted, more stable alkenes are generally formed preferentially by both E1 and E2 mechanisms
 (B) Substrates with a poorer nucleofuge tends to give the less substituted alkenes
 (C) Sterically hindered, bulky bases tend to give the less substituted alkenes
 (D) Reactions by the E1 mechanism are generally less regioselective than those by the E2 mechanism
- o. The reagent used in Gatterman Koch aldehyde synthesis is:
 (A) Pb/BaSO_4 (B) alkaline KMnO_4 (C) acidic KMnO_4 (D) $\text{CO} + \text{HCl}$

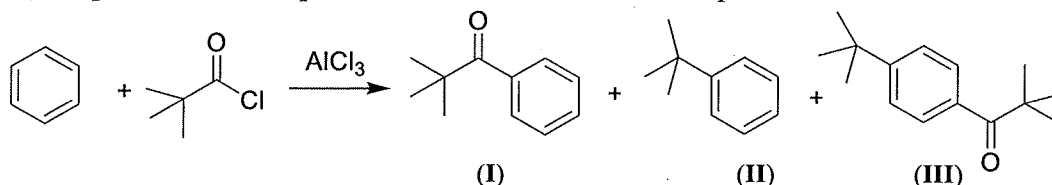
Q2. Attempt **any three** of the following:

(3x5=15)

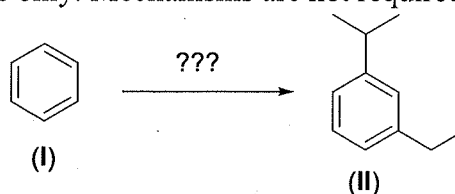
- A. Define electrophilic substitution reactions. What is the fundamental difference between SE_2 and SE_i mechanism?
- B. Discuss the effect of substrate structure and leaving group on the reactivity of electrophilic substitution in aliphatic compounds.
- C. 3-Phenylpropanoyl chloride (I) reacts with $AlCl_3$ to give a ketone of a molecular formula C_9H_8O . Write the probable structure for the ketone with a mechanism of its formation.



- D. Friedel-Craft's acylation of benzene with t -BuCOCl gives ketone (I) and t -butyl benzene (II) as minor products, but the major product is the disubstituted compound (III). Explain how these products are formed with the help of mechanism.



- E. Propose the shortest route for the synthesis of Product (II) from benzene (I). Explain with the help of reactions only. Mechanisms are not required.



Q3. Attempt **any three** of the following:

(3x5=15)

- A. Discuss in detail the stages of free radical substitution reaction between methane and chlorine to produce chloromethane and hydrogen chloride.
- B. Draw the structure of Dibenzoyl peroxide, a radical initiator and describe their homolysis reactions.
- C. Explain the Hunsdieker and the Sandmeyer reactions. What is the free radical intermediate involved in it?
- D. What is the role of NBS (*N*-Bromosuccinamide) in free radical substitutions? Describe the mechanistic approach of NBS with 1-butene?
- E. What is free radical autooxidation of aldehydes? Describe the radical chain reaction mechanism of this reaction?

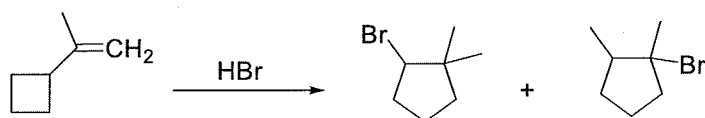
Q4. Attempt **any three** of the following:

(3x5=15)

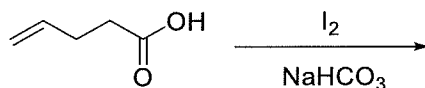
- A. Discuss the mechanism of and applications of Sharpless asymmetric epoxidation?
- B. Write a short note on Mannich and Stobbe reactions.

C. What is the Reformatsky reagent? Explain it with an example and discuss its mechanism in brief?

D. Propose the mechanism of the following reaction.



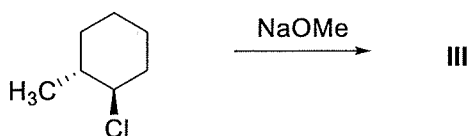
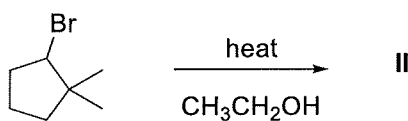
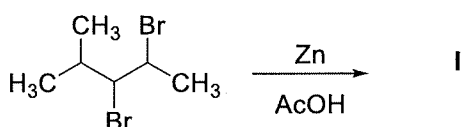
E. What is meant by iodolactonisation? Predict the product of the below reaction and describe its mechanism?



Q5. Attempt *any three* of the following:

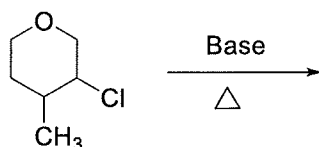
(3x5=15)

A. Write down the products **I**, **II**, and **III** in the following reactions.



B. Describe the mechanism of E1CB reaction with appropriate examples.

C. Write down the possible products in the following transformation. Identify the major product and provide an explanation to support this.



D. The E2 elimination rate constant with $K^+OC(CH_3)_3$ for *cis*-4-*t*-butylcyclohexyl bromide is about 500 times greater than the *trans* isomer. Explain with justification.

E. Write a short note on E1 and E2 elimination reactions based on substrate scope.