B.Sc. DEGREE EXAMINATION – CHEMISTRY

FOURTH SEMESTER

CH 4500 - ORGANIC CHEMISTRY - II

Max. : 100 Marks

Part A

Answer all the questions. 10×2=20

01. Give an evidence for the resonance structure of benzene.
02. What is aldol condensation?
03. Cyclopropane readily undergoes ring-opening reactions. Explain
04. Why is tropylium cation aromatic?
05. What will be the major product formed on dehydrohalogenation of 2-bromo-2,3-dimethylbutane.
06. Name the following alcohols by carbinol and IUPAC system:
    (i) $CH_3–CHOH–CH=CH_2$
    (ii) $CH_3–CH_2–C(CH_3)(OH)–CH_2–CH_2–CH_3$
07. C–O–C bond angle in diethyl ether is greater than H–O–H bond angle in water. Explain.
08. Arrange the following in the order of increasing acidity.
    p-toluic acid, phenyl acetic acid, m-nitrobenzoic acid, benzoic acid.
09. Accont for the lower boiling point and decreasing water solubility of o-nitrophenol as compared with their m- and p- isomers.
10. What is coupling reaction? Give an example.

Part B

Answer any eight questions. 8×5=40

11. Aromatic electrophilic substitution in phenol takes place at ortho and para positions. Explain.
12. Design a synthesis that would convert phenol primarily to a) o-bromophenol b)p-bromophenol.
13. Give the major products of the following reactions with reason.
    a) bromination of p-fluorotoluene
    b) nitration of p-nitrotoluene
14. Explain the stability of cyclohexane on the basis of Sache Mohr theory and the potential energy diagram.
15. Give reasons for the following:
    a) p-chloronitrobenzene has less dipole moment than p-nitrotoluene.
    b) Nitrobenzene and not benzene is used as a solvent for Friedel-Craft's alkylation of bromobenzene.
    c) Halogens are o-p directors but are deactivating.
16. Explain the mechanism of Cannizaro reaction.
17. Explain the mechanism of hydroboration-oxidation of alkenes.
18. Write the mechanism of nitration of methyl phenyl ether.
19. Convert the following:
    i) Phenol into salicylic acid
    ii) Salicylic acid into α-chloro benzoyl chloride.
20. Explain Gabriel phthalimide synthesis. How would you use this method in the preparation of glycine and n-propyl amine?

21. What is diazodisation? How is benzene diazonium chloride prepared? Give its mechanism.
22. Discuss the mechanism of pinacol-pinacolone rearrangement.

Part C

Answer any four questions. 4×10=40

23. a) Explain the mechanism of formation of 2,4-dinitrophenylhydrazone derivative from acetone.

    b) Compound A with the molecular formula $C_5H_8O_2$ on reduction forms n-pentane and forms dioxime with hydroxylamine. It gives positive test with Tollen's reagent and also forms iodoform. Suggest a suitable structure of the compound.

24. a) Two isomeric hydrocarbons A and B have molecular formula C_8H_{10}. A on oxidation gives benzoic acid while a dicarboxylic acid is formed by the oxidation of B which later on heating forms anhydride. Suggest the structures of A and B.

    b) CH_3-CH (X) - CH_2- CH_2- CH_3 on dehydrohalogenation forms 2-pentene and 1-pentene. The major and minor product varies with respect to the substituents. Explain the reactions with reason.

Substituents	2-pentene	1-pentene
Br	80%	20%
Cl	75%	25%
F	65%	35%
S^+R_2	30%	70%
N^+R_3	30%	70%

25. a) When nitrobenzene is nitrated m-dinitrobenzene is formed as the major product whereas anisole on nitration forms a mixture of o- and p-nitro compounds. Explain.

    b) How are the following conversions done?

    i) phenol to cyclohexane

    ii) cyclopropane to butanoic acid. (6+2+2)

26. i) Explain the mechanism of Reimer-Tiemann's reaction. (4+6)

    ii)Identify the products (A, B, C and D) in the following sequence of reactions.

$$\text{Isopropyl alcohol} \xrightarrow{K_2Cr_2O_7/H_2SO_4} A \xrightarrow{MeMgBr} B \xrightarrow{H_3O^+} C \xrightarrow{High\ Pressure} D$$

27. a)Write any two methods of preparation of each primary, secondary and tertiary amines. (6)

    b)Phenol is less acidic than trinitrophenol and carboxylic acids. Explain. (4)

28. a) Explain the mechanism of Hofmann rearrangement. (6)

    b) How will you convert phenol into salicylaldehyde? Give the mechanism. (4)

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PART-A

*Answer **ALL** questions.* (10 × 2 = 20)

01. 'Cyclopropane is more reactive than cyclohexane'. Why?
02. What are the conformers possible for cyclohexane? Which one is more stable? Why?
03. How would you distinguish methanol from ethanol by means of chemical tests?
04. 'Williamson's synthesis is useful for the preparation of both simple and mixed ethers'. Justify this statement with suitable examples.
05. Arrange the following in the increasing order of their acidity. Justify your answer. Monochloroacetic acid, Dichloroacetic acid, Acetic acid, Formic acid and Trichloro acetic acid.
06. What happens when maleic acid is treated with bromine? Identify the stereochemistry of the product obtained?
07. Name the electrophile in nitration of benzene. What are the evidences for its existence?
08. 'Aniline does not undergo Friedel-Craft's reaction'. Why?
09. How would you prepare the following from benzene diazonium chloride? (i) Benzene and (ii) Benzoic acid
10. Give the mechanism of Reimer-Tiemann reaction.

PART-B

*Answer **any EIGHT** questions.* (8 × 5 = 40)

11. Explain Baeyer's strain theory in the stability of cycloalkanes.
12. How are alcohols prepared from hydroboration-oxidation method? Explain with mechanism.
13. An amide(A) having molecular formula C_3H_7ON on hydrolysis gives an acid $C_3H_6O_2$(B). (B) on chlorination in the presence of red phosphorus produces a chloroacid(C).The latter on boiling with aqueous NaOH and subsequent acidification forms lactic acid(D).Write the reactions and identify the structure of A, B, C and D.
14. What happens when benzaldehyde is heated with alcoholic KCN solution? Explain the mechanism.
15. How would you prepare 4-methylpentanoic and 3-methylbutanoic acid using diethyl malonate?
16. Explain the mechanism of Hofmann-bromamide reaction. Name the intermediate in this reaction.
17. 'Nitration of benzene is irreversible while sulphonation of benzene is a reversible reaction.' Explain.
18. What are sulpha drugs? Explain the mechanism of action of sulpha durgs.
19. What happens when 3-bromo-2, 3-dimethyl pentane is treated with alcoholic KOH? Identify the different products obtained and explain with mechanism.
20. Explain the mechanism of Baeyer-Villiger rearrangement.
21. Explain the synthetic utility of acetoacetic ester with examples.
22. Explain aromaticity, antiaromaticity and nonaromaticity with suitable examples.

PART-C

*Answer **any FOUR** questions.* (4 × 10 = 40)

23. a) Explain the mechanism of reduction of $CH_3COOC_2H_5$ by $LiAlH_4$.
    b) Compare the stereochemistry of products obtained in S_N1 and S_N2 reactions.
24. a) How are Grignard reagents used in the preparation of primary, secondary and tertiary alcohols? Explain with suitable examples.
    b) Explain the mechanism of preparation of ethers by oxymercuration- demercuration method.
25. a) How are the following compounds prepared?
        (i) acrylic acid (ii) cinnamic acid (iii) maleic acid
    b) Explain the action of heat on α-, β- and γ-hydroxy acids and identify the products obtained.
26. a) Explain the mechanism of sulphonation of benzene
    b) 'Halogens are deactivating groups but o-, p- directing'. Explain.
27. a) How will you synthesise the following compounds from benzaldehyde?
        (i) Mandelic acid (ii) m-Benzaldehydesulphonic acid
    b) Write a note on: (a) Cannizaro reaction (b) Perkin reaction
28. a) Explain Claisen and abnormal Claisen rearrangements with mechanism.
    b) How would you convert m-nitrophenol from nitrobenzene? Explain all the steps involved in this process.

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