Serial No. 0011021 A–IGQ–O–FGC

CHEMISTRY

Paper—III

Time Allowed : Three Hours *Maximum Marks · 200*

INSTRUCTIONS

Please read each of the following instructions carefully before attempting questions :

*There are **TWELVE** questions divided under **TWO** Sections.*

*Candidate has to attempt **TEN** questions in all.*

*Attempt any **FIVE** questions from each of the **TWO** Sections A and B including question no. **1** (Section A) and question no. 7 (Section B) which are compulsory.*

The number of marks carried by a question / part is indicated against it.

All parts and sub-parts of a question are to be attempted together in the answer book.

Attempts of questions shall be counted in chronological order. Unless struck off, attempt of a question shall be counted even if attempted partly.

Any page or portion of the page left blank in the answer book must be clearly struck off.

*Answers must be written in **ENGLISH** only.*

Neat sketches are to be drawn to illustrate answers, wherever required.

Unless other-wise mentioned, symbols and notations have their usual standard meanings.

Assume suitable data, if necessary and indicate the same clearly.

SECTION—A

(Attempt any **FIVE** questions including question no. **1** which is compulsory.)

1. Answer **ALL** of the following : $5 \times 8 = 40$

(a) Suggest an analytical method for the quantitative estimation of Fe_2O_3, Al_2O_3 and TiO_2 in naturally occurring bauxite. 5

(b) 500 mg of $ZnSO_4\ 7H_2O$ was placed in a 250 ml standard volumetric flask and was dissolved in water, the volume of the solution was made up to 250 ml. Express the concentration of Zinc (Zn) in terms of :

(i) Normality

(ii) Molarity

(iii) Molality

(iv) Formality

(v) ppm. 1×5

(c) What will be the concentration of Pb^{+2} in Saturated solution of $PbBr_2$ in water Saturated solution of $PbBr_2$ in which $[Br^-]$ is somehow fixed at 0.10 M ? 2.5×2

(d) What are primary standards ? Can an accurately weighed $KMnO_4$ dissolved in an exact volume of water be treated as a standard solution ? Justify your answer. 5

(e) Define the following :

(i) Accuracy

(ii) Precision

(iii) Standard Deviation

(iv) Determinant error

(v) Indeterminant error. 1×5

(f) What is the difference between combustion and pyrolysis ?

Write a balanced equation for the combustion of $C_8H_7NO_2SBrCl$ in a C, H, N, S elemental analyser. 2.5×2

(g) How does the column temperature affect the performance of the separation in chromatography ?

Describe a method for the determination of number of plates in a chromatographic column. 2.5×2

(h) How can you estimate the water content of a petroleum sample ? 5

2. 7+8=15

(a) Cubic crystals are formed by copper. When they were shined with X-rays from a copper target (wave length 1.5405 Å), reflections were found at 43.30, 50.42, 74.12, 89.92, 95.16° and other higher angles.

(i) Determine the type of lattice formed by copper.

(ii) What is the unit cell length at room temperature ? 3.5×2

(Contd.)

(b) What is the equivalence volume, Ve, in the titration of 100.0 mL of 0.100 M cocaine ($K_b = 2.6 \times 10^{-6}$) with 0.20 M HNO_3 ?

Calculate the pH of the solution after the addition of following volumes of acid, Va :

Va = 0.0, 10, 20, 25, 30, 40, 49, 49.9, 50, 50.1, 51.0 and 60 mL.

Draw a graph of pH versus volume of the acid added, Va. 8

3. 10+5=15

(a) What do you understand by plate height in a chromatographic column ?

What would be the effect of the following on the plate height of a column ?

(i) Increasing the flow rate

(ii) Decreasing the rate of sample injection

(iii) Reducing the particle size of the packing

(iv) Increasing the injection port temperature

(v) Increasing the weight of the stationary phase. 5+5

(b) Write a balanced equation for the redox reaction involving ferrous ammonium sulphate and potassium permanganate solution in acidic medium. 5

4. 7+8=15

(a) What is skin effect ?

Discuss the advantages of ICP over flame AES arising due to the skin effect. 7

(b) 700 mg of a sample containing Fe(III) was dissolved in 20 ml of 0.0500 M EDTA solution. The unreacted EDTA was titrated with 0.0420 M (Cu) solution, total volume of Cu(II) solution consumed was equal to 5.08 ml.

Calculate the amount of Fe(III) in the sample, report your result as % of Fe_2O_3 in the sample. 8

5. 5+10=15

(a) Why is atomic emission more sensitive to flame instability than atomic absorption ? 5

(b) What is the function of flame in flame photometry and in atomic absorption spectrometry ? 3+3

What is the purpose of using an internal standard in flame emission method of analysis ? 4

6. 10+5=15

(a) Solid residue weighing 8.4448 g from an aluminium refining process was dissolved in an acid to give Al^{+3} in solution.

The solution was treated with 8-hydroxy quinoline to precipitate Al (8-hydroxy quinoline)$_3$ which was ignited to give Al_2O_3 weighing 0.8554 g.

Calculate the weight percentage of Al in the original mixture. 10

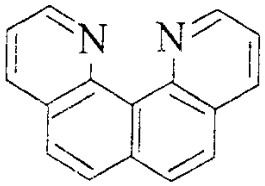
(b) What is the importance of Lambert-Beer's law in quantitative analysis ? What are its limitations ? 5

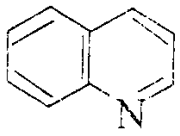
SECTION—B

(Attempt any **FIVE** questions including question no. 7 which is compulsory.)

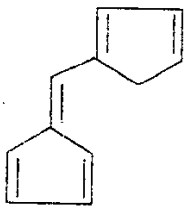
7. Answer **ALL** of the following : $4 \times 10 = 40$

(a) Explain why quino [7, 8-h] quinoline is a stronger base than quinoline, whereas quinoline is a stronger nucelophile between the two. 4

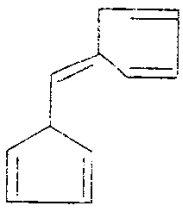




(b) Which of the following molecules would you expect to absorb at a longer wavelength in the UV region ? Explain your answer. 4

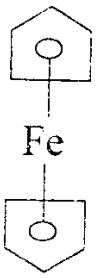


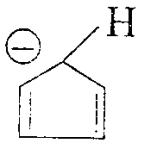
A

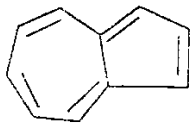


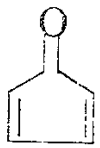
B

(c) Explain Huckel's rule for aromaticity. Identify the compound which is not aromatic among the following and explain why. 4









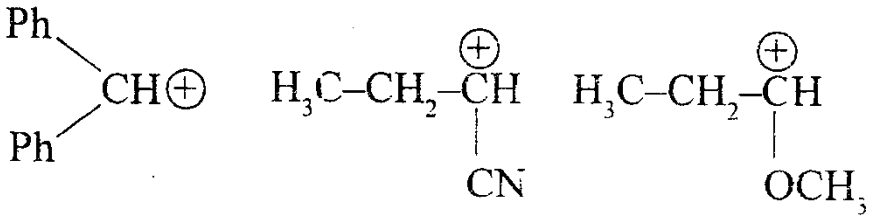
(Contd.)

(d) Explain why cyanide ion is a specific catalyst in benzoin condensation and the reaction fails when attempted with p-nitrobenzaldehyde. 4

(e) Tell precisely how you would use the proton NMR spectra to distinguish between the following pairs of compounds (i) Ethyl acetate and methyl propionate and (ii) Propanal and propanone. 4

(f) Illustrate the application of Gabriel's phthalimide synthesis in the preparation of 1, 2-diaminoethane from corresponding dihalide. 4

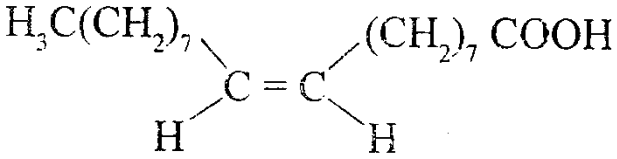
(g) Predict the stability order of the following carbocations. Briefly explain your reasoning : 4



A **B** **C**

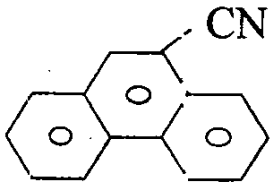
(h) Propose appropriate reagents/catalysts for the following reductions : 4

(A) $CH_3(CH_2)_7C \equiv C(CH_2)_7COOH \xrightarrow{?}$



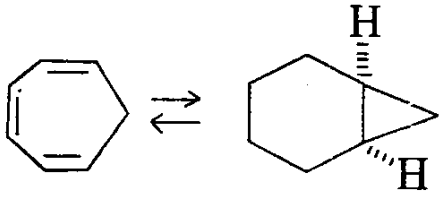
(B) $C_6H_5CH=CHNO_2 \xrightarrow{?} C_6H_5CH_2CH_2NO_2$

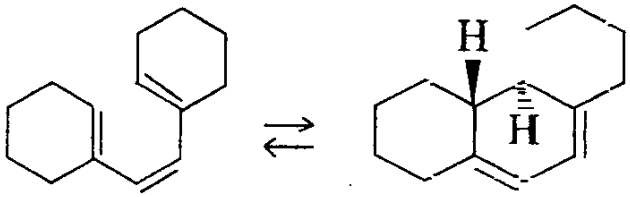
(i) Predict the products in the following : 4

(A)  $+ CH_3Mg^- \rightarrow \xrightarrow{H_3O^+} ?$

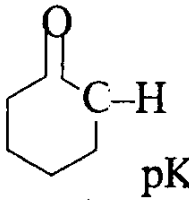
(B) $PhC \equiv CMgBr + (CH_3CO)_2O \rightarrow \xrightarrow{H_3O^+} ?$

(j) Identify the mode of cyclization and the pathway, thermal or photochemical, involved in each of the following electrocyclic reactions : 4

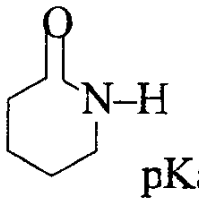
(A) 

(B) 

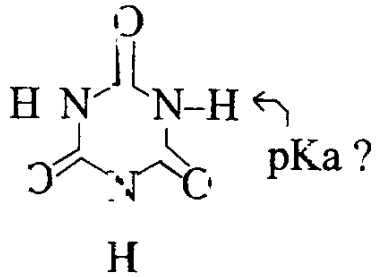
8. (a) Using the given pKa values as a guide, estimate the approximate pKa for N-H bond of cyanuric acid tautomer A. Briefly justify your answer. 5



pKa 19



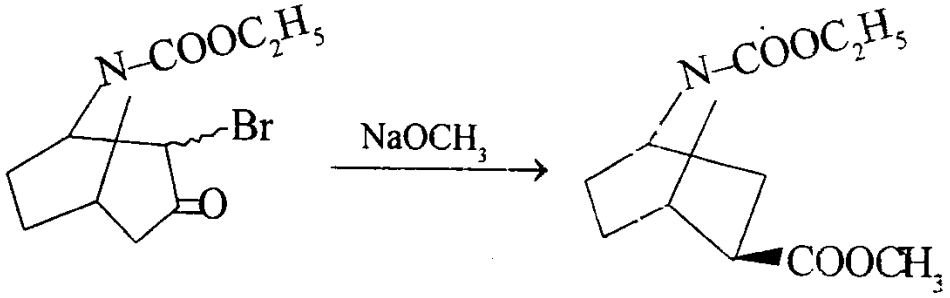
pKa 16



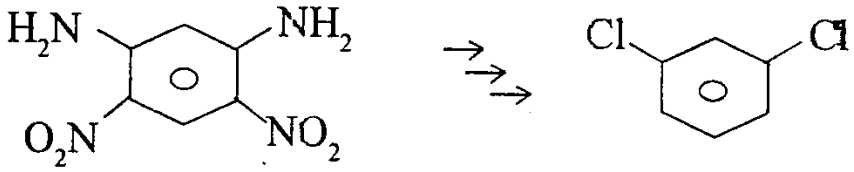
Cyanuric acid tautomer A

(Contd.)

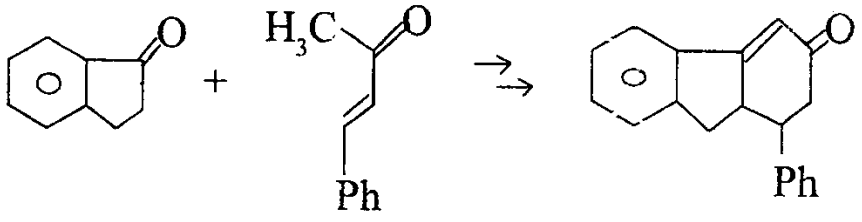
(b) Identify the name reaction and propose mechanism for the following reaction : 5



(c) Suggest a reaction sequence that would permit synthesis of the aromatic compound shown below : 5

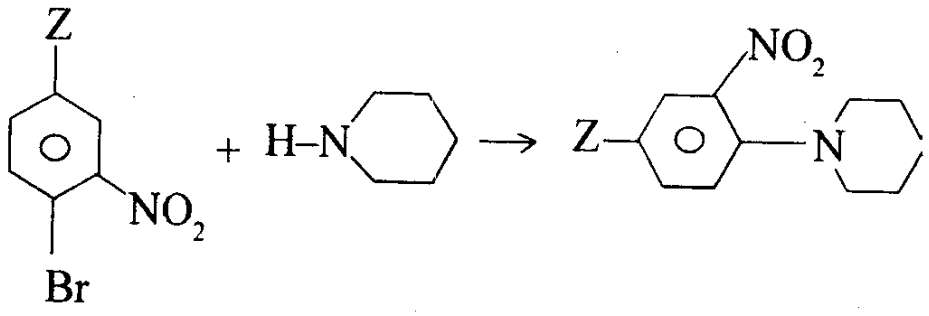


9. (a) Give sequence of reactions, with mechanism, for the following conversion : 5



(Contd.)

(b) Predict the effect of substituent Z on the relative rates in the following reaction. Also give the mechanism involved. 5



A : Z = NO_2 and B : Z = OCH_3

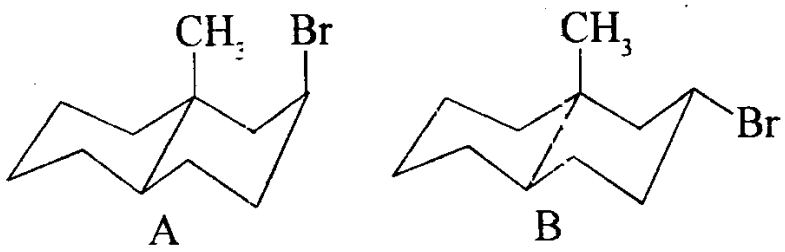
(c) Give the advantages of stork enamine alkylation over direct base catalysed alkylation of aldehydes and ketones. Predict the major product of methylation with CH_3I of 2-methylcyclohexanone via pyrrolidine enamine. 5

10. (a) Given below are the relative reactivities of various hydrogen atoms of n-butylchloride towards further photochlorination. Account for the striking difference in the reactivity of hydrogens towards photochlorination. 5

$$\underset{8}{H_3C}—\underset{17}{CH_2}—\underset{5.5}{CH_2}—\underset{1}{CH_2}—Cl$$

(b) What are the stereoelectronic requirements of E-2 elimination reactions ? Which of the following

two isomers would be expected to undergo base-catalysed dehydrohalogenation at a faster rate ? Explain your answer. 5

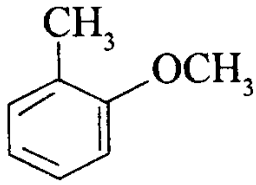


(c) Give HOMO and LUMO orbitals of 1, 3-butadiene, 1, 3, 5-hexatriene, allyl cation and allyl anion in ground state. 5

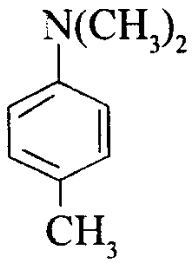
11. (a) Discuss important similarities and differences between conjugation and aromaticity. 5

(b) Show by construction of orbital symmetry correlation diagram whether CON or DIS rotatory mode of cyclization is symmetry allowed for 1, 3-butadiene via photochemical pathway. 5

(c) Complete the following equations : 5

(A) 

$\xrightarrow[C_2H_5OH]{Li,\ NH_3}$ X $\xrightarrow[\text{hydrolysis}]{\text{acid}}$ Y

(B) 

$\xrightarrow[t\text{-}C_4H_9OH]{Li,\ NH_3}$ Z $\xrightarrow[\text{hydrolysis}]{\text{acid}}$ Z – 1

12. (a) Determine the structure of an organic compound with molecular formula $C_{11}H_{12}O_2$ which shows the following spectral data : 5

IR (cm^{-1}) : 1720, 1600, 1580, 770, 710

PMR (δ ppm) : 1.3 (t, 3H) (J = 7.00 Hz), 4.2 (q, 2H) (J = 7.00 Hz), 6.3 (d, 1H) (J = 16 Hz), 7.3 (m, 5H), 8.5 (d, 1H) (J = 16 Hz).

(b) What is McLafferty rearrangement in mass spectrometry ? Mass spectrum of 1-phenylbutanone exhibits m/e (mass by charge) 105 as the base peak and m/e 120 as one of the major peaks. Account for the same. 5

(c) Give mechanism involved in Wittig reaction. Phosphorane, $(C_6H_5)_3P = CHCOOC_2H_5$, reacts rapidly with aldehydes but with ketone the reaction is sluggish. Explain why. 5