

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 : 5×8=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 $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ 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 $[\text{Br}^-]$ 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 \AA), reflections were found at 45.30 , 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

- (b) What is the equivalence volume, V_e , 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, V_a :

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

Draw a graph of pH versus volume of the acid added, V_a . 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 $\text{Al}(\text{8-hydroxy quinoline})_3$ 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 ?

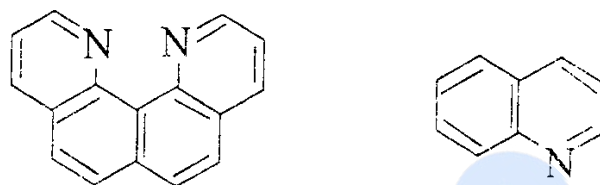
5

SECTION—B

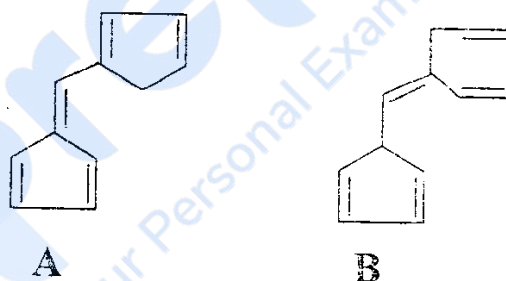
(Attempt any FIVE questions including question no. 7 which is compulsory.)

7. Answer ALL of the following : 4×10=40

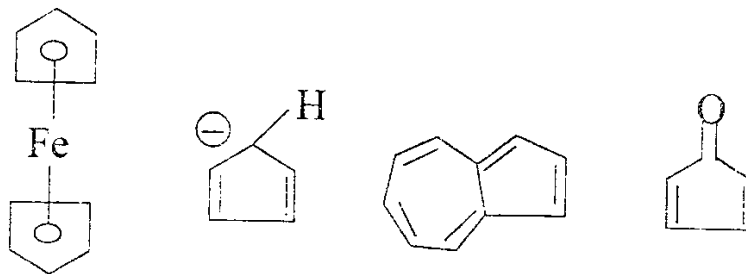
- (a) Explain why quino [7, 8-h] quinoline is a stronger base than quinoline, whereas quinoline is a stronger nucleophile between the two. 4



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



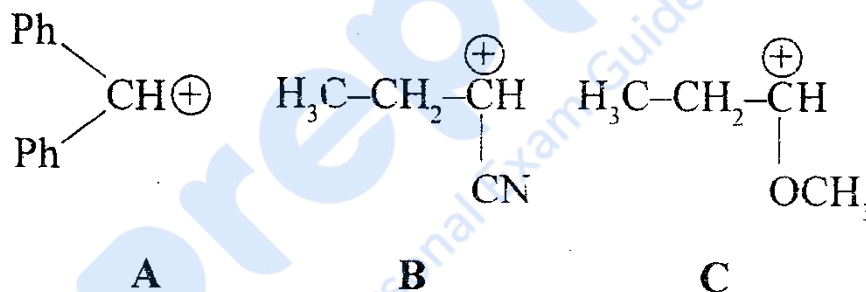
- (c) Explain Huckel's rule for aromaticity. Identify the compound which is not aromatic among the following and explain why. 4



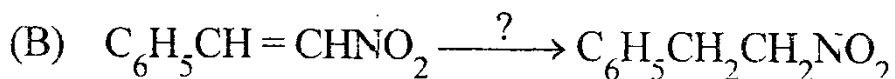
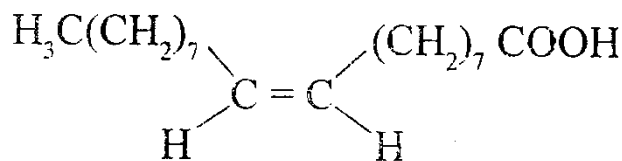
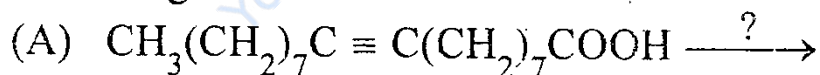
6
x

(Contd.)

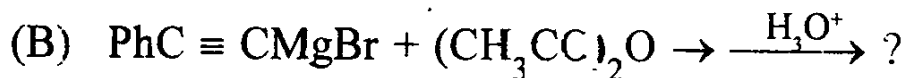
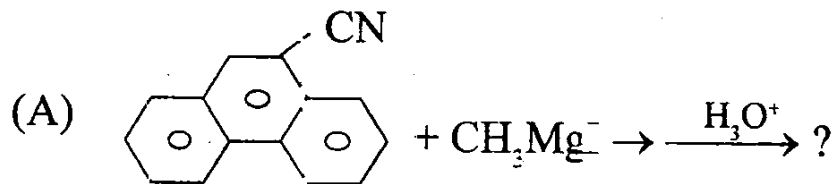
- (d) Explain why cyanide ion is a specific catalyst in benzoin condensation and the reaction fails when attempted with p-nitrobenzaldehyde. 4
- (e) Tell precisely how you would use the proton NMR spectra to distinguish between the following pairs of compounds (i) Ethyl acetate and methyl propionate 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



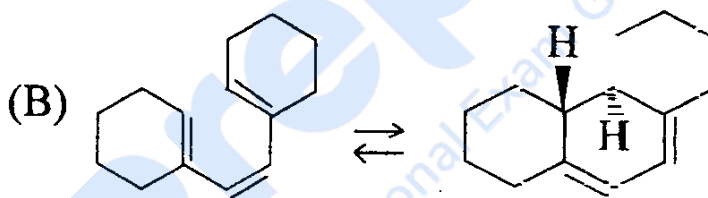
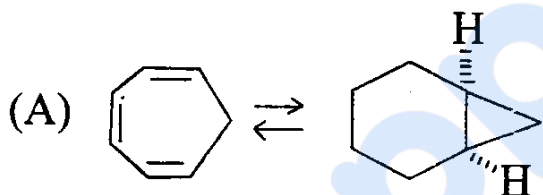
- (h) Propose appropriate reagents/catalysts for the following reductions : 4



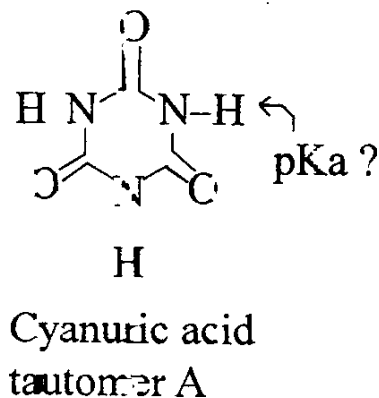
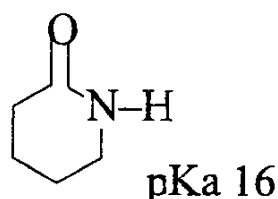
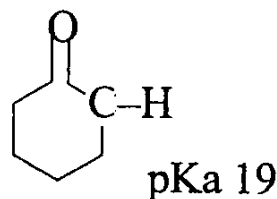
(i) Predict the products in the following : 4



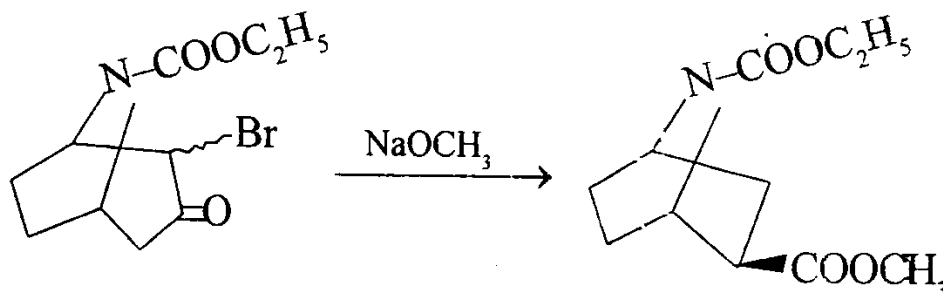
(j) Identify the mode of cyclization and the pathway, thermal or photochemical, involved in each of the following electrocyclic reactions : 4



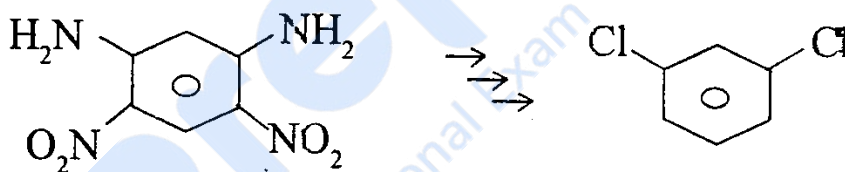
8. (a) Using the given pKa values as a guide, estimate the approximate pKa for N-H bond of cyanuric acid tautomer A. Briefly justify your answer. 5



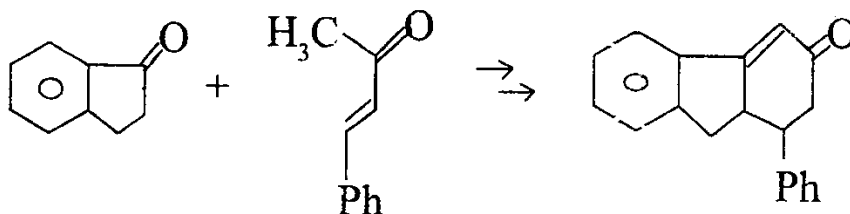
- (b) Identify the name reaction and propose mechanism for the following reaction : 5



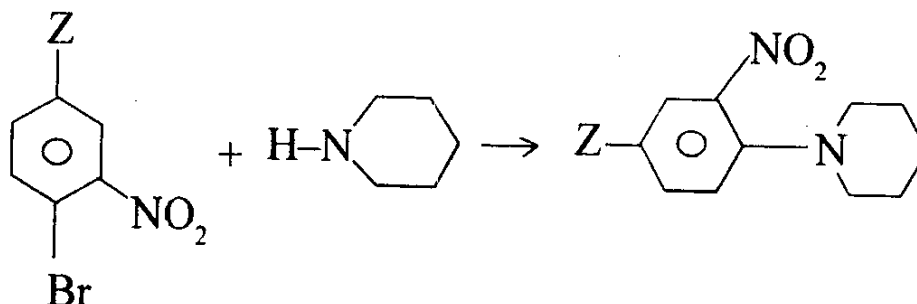
- (c) Suggest a reaction sequence that would permit synthesis of the aromatic compound shown below : 5



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

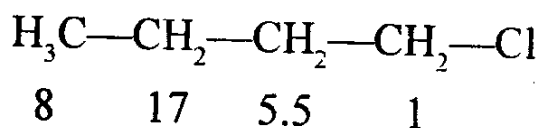


- (b) Predict the effect of substituent Z on the relative rates in the following reaction. Also give the mechanism involved. 5



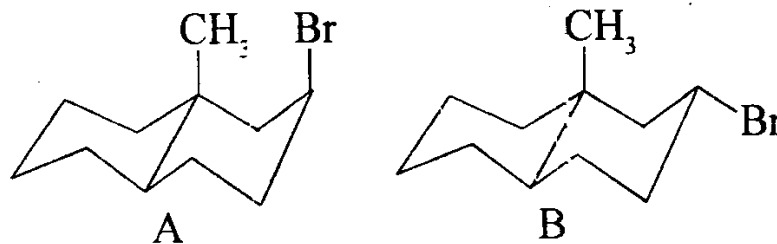
A : Z = NO₂ and B : Z = OCH₃

- (c) Give the advantages of stork enamine alkylation over direct base catalysed alkylation of aldehydes and ketones. Predict the major product of methylation with CH₃I 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

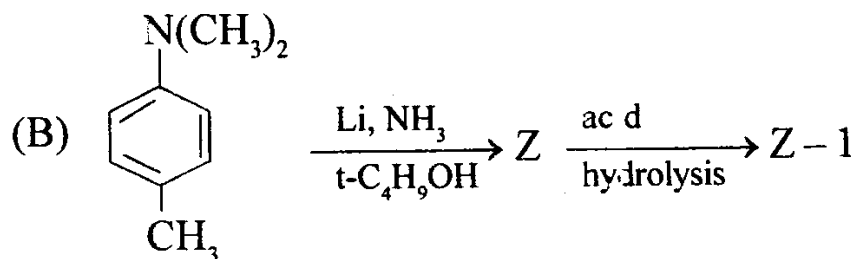
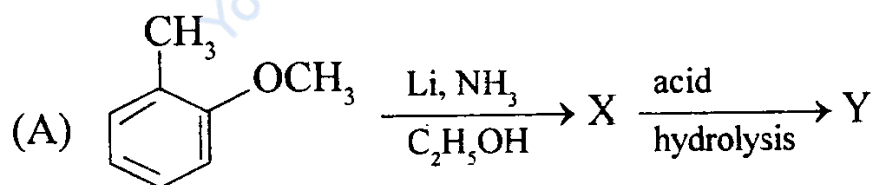


- (b) What are the stereoelectronic requirements of E-2 elimination reactions? Which of the following

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



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

prepp
Your Personal Exam Guide