

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  $\text{Fe}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3$  and  $\text{TiO}_2$  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  $\text{Pb}^{+2}$  in Saturated solution of  $\text{PbBr}_2$  in water Saturated solution of  $\text{PbBr}_2$  in which  $[\text{Br}^-]$  is somehow fixed at 0.10 M ? 2.5×2
- (d) What are primary standards ? Can an accurately weighed  $\text{KMnO}_4$  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 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  $\text{HNO}_3$  ?

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  $\text{Fe}_2\text{O}_3$  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  $\text{Al}^{+3}$  in solution.

The solution was treated with 8-hydroxy quinoline to precipitate  $\text{Al}(\text{8-hydroxy quinoline})_3$  which was ignited to give  $\text{Al}_2\text{O}_3$  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 ?

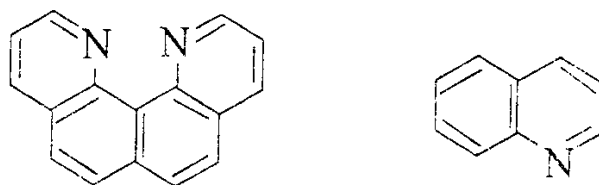
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SECTION—B

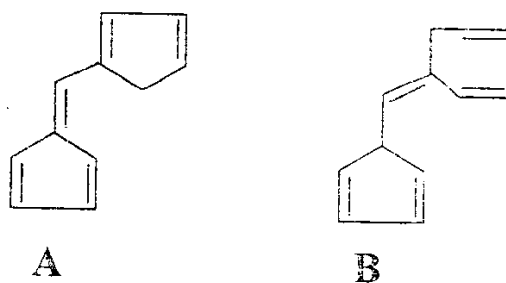
(Attempt any FIVE questions including question no. 7 which is compulsory.)

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

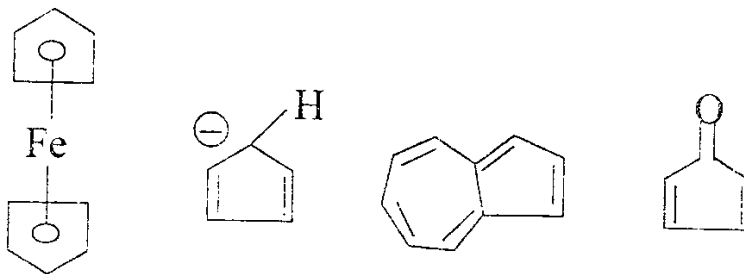
- (a) Explain why quino [7, 8-h] quinoline is a stronger base than quinoline, whereas quinoline is a stronger nucleophile between the two. 4



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



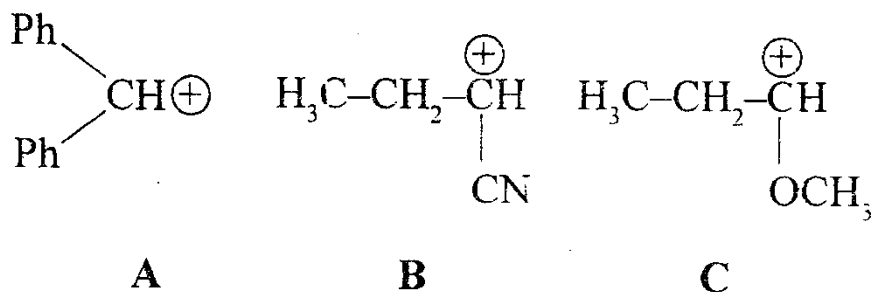
- (c) Explain Huckel's rule for aromaticity. Identify the compound which is not aromatic among the following and explain why. 4



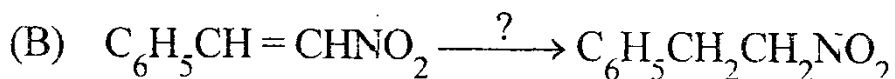
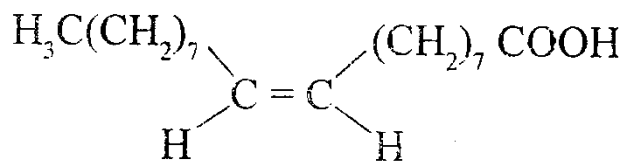
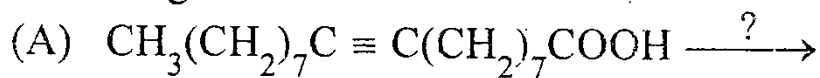
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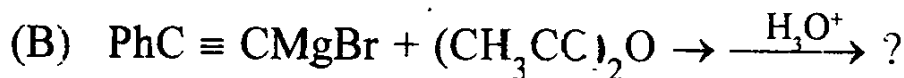
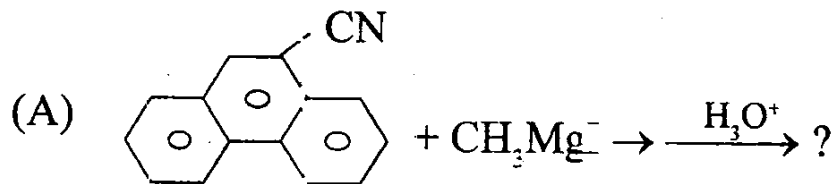
- (d) Explain why cyanide ion is a specific catalyst in benzoin condensation and the reaction fails when attempted with p-nitrobenzaldehyde. 4
- (e) Tell precisely how you would use the proton NMR spectra to distinguish between the following pairs of compounds (i) Ethyl acetate and methyl propionate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



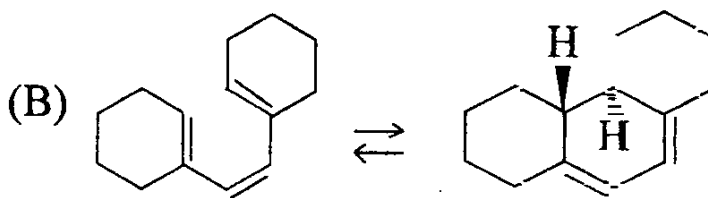
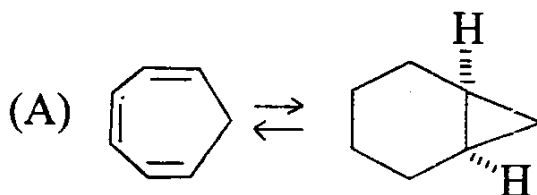
- (h) Propose appropriate reagents/catalysts for the following reductions : 4



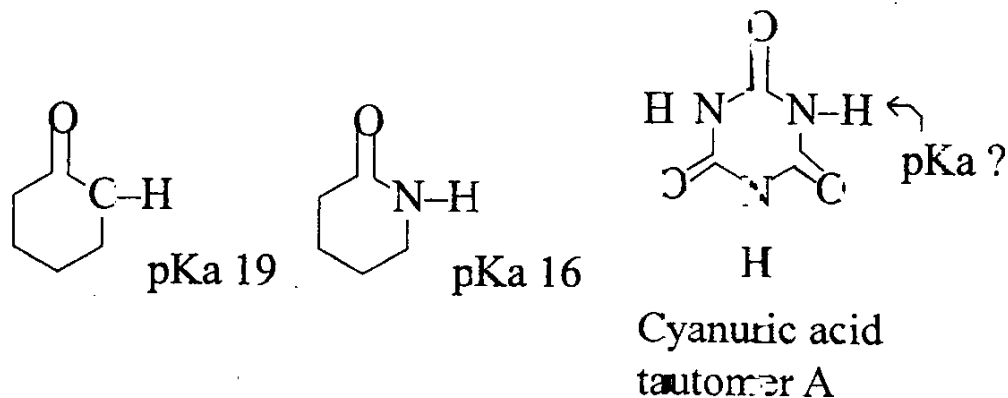
(i) Predict the products in the following : 4



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

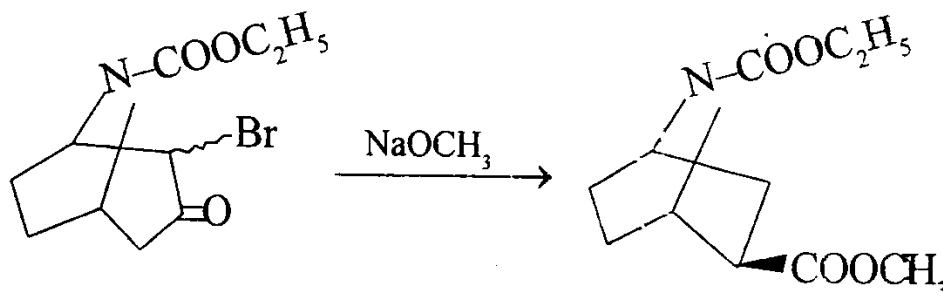


8. (a) Using the given pKa values as a guide, estimate the approximate pKa for N-H bond of cyanuric acid tautomer A. Briefly justify your answer. 5

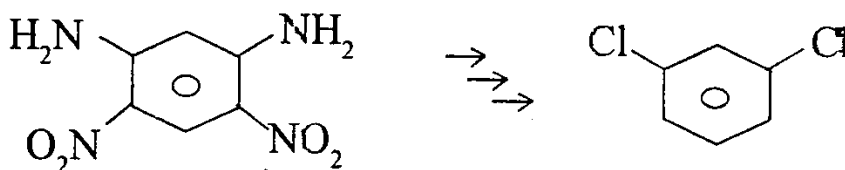




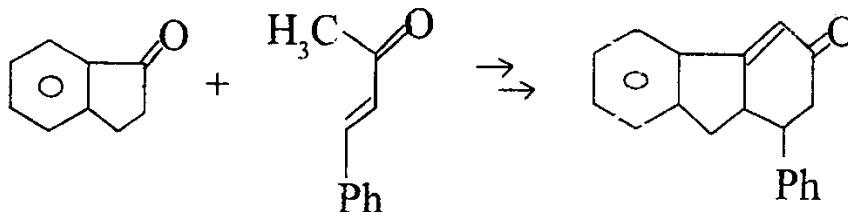
- (b) Identify the name reaction and propose mechanism for the following reaction : 5



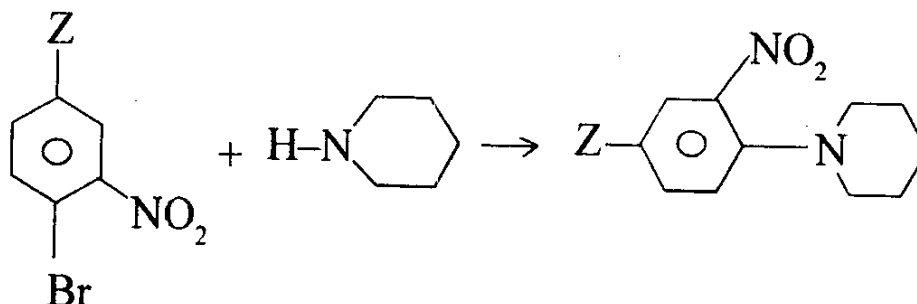
- (c) Suggest a reaction sequence that would permit synthesis of the aromatic compound shown below : 5



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

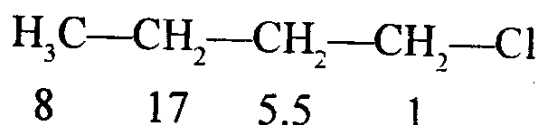


- (b) Predict the effect of substituent Z on the relative rates in the following reaction. Also give the mechanism involved. 5



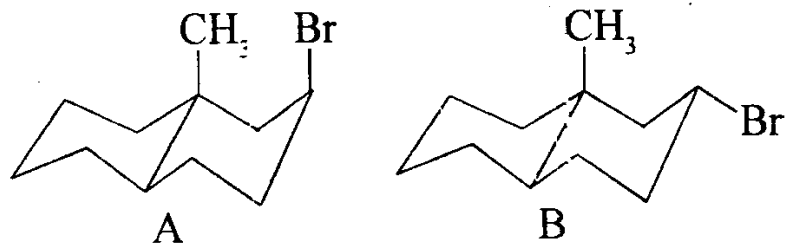
A : Z = NO<sub>2</sub> and B : Z = OCH<sub>3</sub>

- (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<sub>3</sub>I 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

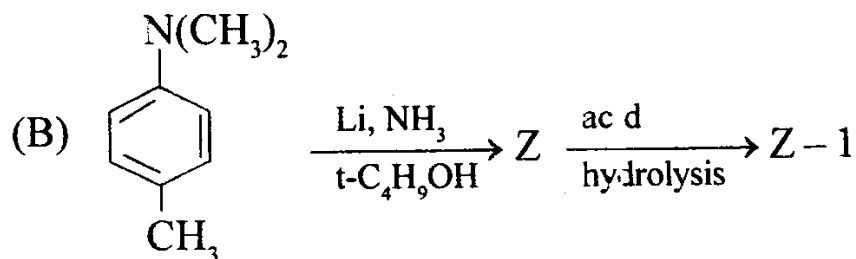
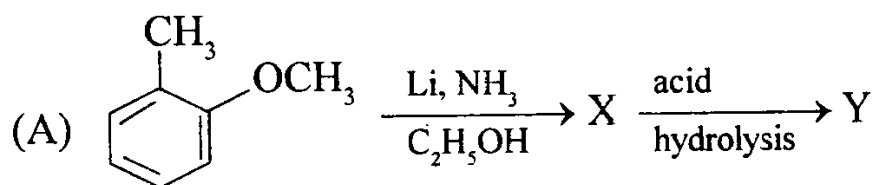


(c) Give HOMO and LUMO orbitals of 1, 3-butadiene, 1, 3, 5-hexatriene, allyl cation and allyl anion in ground state. 5

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 ( $\delta$  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

