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FOR UPSC CGGE EXAM PREPARATION

UPSC CGGE 2024 Question Paper · Chemistry Paper III

EXAM	YEAR	TYPE	SUBJECT
UPSC CGGE	2024	Question Paper	Chemistry Paper III

DETAILS

Mains

Combined Geo-Scientist (Main) Examination, 2024

SGSE–B–CMS

CHEMISTRY

PAPER—III

Time Allowed : Three Hours	Maximum Marks : 200

QUESTION PAPER SPECIFIC INSTRUCTIONS

Please read each of the following instructions carefully before attempting questions

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

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

Question No. **1** in Section—A and Question No. **6** in Section—B are compulsory. Of the remaining questions, candidates have to answer **FOUR** questions, choosing **TWO** from each Section.

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

Neat sketches are to be drawn to illustrate answers, wherever required. These shall be drawn in the space provided for answering the question itself.

Unless otherwise mentioned, symbols and notations have their usual standard meanings.

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

Attempts of questions shall be counted in sequential 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 Question-cum-Answer (QCA) Booklet must be clearly struck off.

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

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SECTION—A

1. *(a)* A weighing balance showed the weight of a substance 9·5 g, which is 0·5 g lower than its actual weight. Calculate % relative error. 5

(b) What do you mean by partition ratio (k') and relative retention (α) in chromatography? 5

(c) A $4 \cdot 00 \times 10^{-4}$ M solution of aminobenzene in water has absorbance, $A = 0 \cdot 504$ at 280 nm in a 1·00 cm cell. What will be the transmittance of a $1 \cdot 50 \times 10^{-3}$ M solution of aminobenzene in water measured at the same wavelength but in a 0·5 cm cell? 5

(d) A thermogram of a magnesium compound showed a loss of 66·0 mg from a total of 126·5 mg used for the analysis. Identify the compound either as MgO or $MgCO_3$ or MgC_2O_4. [Mg = 24·3, C = 12, O = 16] 5

(e) What are the properties vital for detectors to be used in X-ray fluorescence instrument? 5

(f) How does plasma generate in inductively coupled plasma (ICP) technique? 5

(g) What do you understand by the calorific value of a fuel? 5

(h) Differentiate between AAS and ICP techniques based on the properties like accuracy, interferences and detection limit. 5

2. *(a)* What is Bonner affinity series in ion-exchange chromatography? Which factors govern this series? 10

(b) What is the role of monochromator in IR spectroscopy? Explain the types and components of monochromator. 10

(c) How does the furnace atmosphere affect the shape of the TG curve? Specify at least two reasons. Compare the thermodecomposition profiles of $CaC_2O_4 \cdot H_2O$ taken in dry O_2(g) and in dry N_2(g). 10

3. *(a)* What is X-ray diffraction qualitative phase analysis? How is it measured? Mention its major applications. 10

(b) What are the important components of inductively coupled plasma (ICP)? Explain the functioning of sampler-skimmer system. 10

(c) What do you mean by theoretical oxygen demand (ThOD)? Determine the volume of the air needed for complete combustion of 1 m^3 of producer gas having composition by volume H_2 = 30%, CO = 10%, CH_4 = 4%, N_2 = 56%. 10

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4. *(a)* What is plate height (H)? Calculate the number of plates in the column resulting in chromatographic peak with $t_R = 52 \cdot 3$ sec and $W_{1/2} = 5 \cdot 3$ mm. Also comment on the efficiency of the column.

Given : $N = 5 \cdot 545 \left(\frac{t_R}{W_{1/2}} \right)^2$ 10

(b) List out the interferences in flame photometry and describe the ways to eliminate at least two of them. 10

(c) How are X-rays detected? Explain the various types of X-ray detectors. 10

5. *(a)* A set of seven measured values resulted in $\overline{X} = 14 \cdot 74 \, (\pm 0 \cdot 38)$. Calculate the confidence interval including the true value at a confidence level (CL) of 99·0%.

[Given : $t_{99.0}$ (degrees of freedom) : 4·604(4), 4·032(5), 3·707(6), 3·499(7)] 5

(b) *(i)* Calculate the wavelength of the resonance line of sodium atom, if the excitation energy of the resonance level is 2·10 eV.

[Given : $hc = 12330$] 5

(ii) 2·00 mL of the urine sample A was treated with reagent to generate colour with phosphate, and the resulting content was diluted to 100 mL. A second 2·00 mL sample B of the same urine was added to exactly 5·0 mL of phosphate solution (0·0300 mg/mL), which was treated in the same way as the sample A. The absorbance of the solution from $A = 0 \cdot 428$, and that from $B = 0 \cdot 538$. Calculate the concentration of phosphate (mg/mL) in the urine sample A. 5

(c) *(i)* State the ultimate analysis of a fuel. Write the basic principle of the method used for the analysis of nitrogen content in a fuel. 10

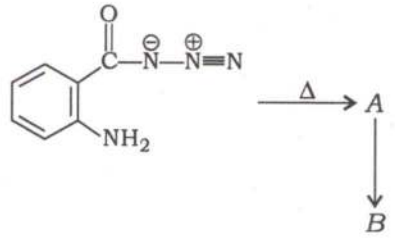
(ii) An ore sample of Fe_3O_4 weighing 1·3155 g was dissolved in HCl, and treated with HNO_3 to convert all iron into Fe^{3+} state. The resulting content was then diluted with water, followed by addition of NH_3 (excess) to precipitate Fe^{3+} into $Fe(OH)_3$ · Ppts were filtered, washed with water and ignited to give the residue of pure Fe_2O_3 weighing 0·7273 g. Calculate % w/w Fe_3O_4 in the ore sample.

[$Fe_2O_3 = 159 \cdot 70$, $Fe_3O_4 = 231 \cdot 54$] 5

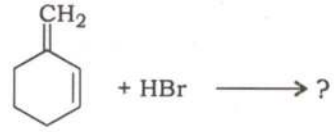
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SECTION—B

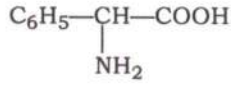
6. *(a)* Complete the following reaction and identify the products *A* and *B* : 4



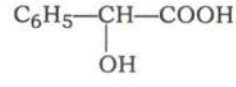
(b) Predict the product(s) of the following reaction. Which product will be major and why? 4



(c) How will you prepare the compounds (*I*) and (*II*) from benzaldehyde using suitable reagents? 4

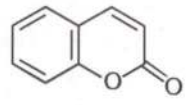


(*I*)

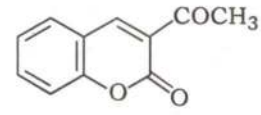


(*II*)

(d) Suggest the suitable starting materials and conditions to synthesize the following compounds *A* and *B* : 4

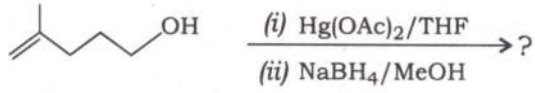


A

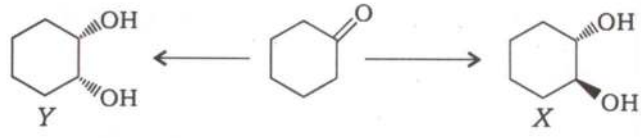


B

(e) Give the product and mechanism of the following reaction : 4

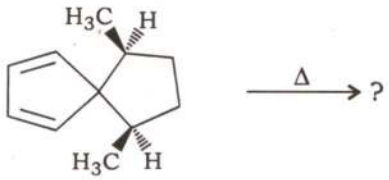


(f) How will you synthesize the compounds *X* and *Y* from cyclohexanone by using suitable reagents? 4



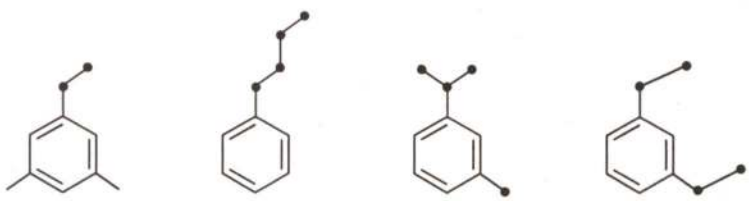
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(g) Complete the following reactions and indicate how they are formed : 4

(i) 

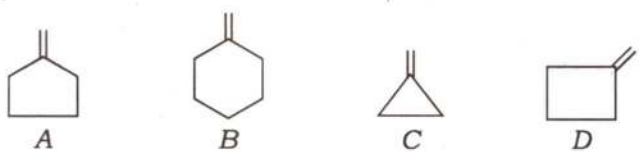
(ii) 

(h) An organic compound with molecular formula $C_{10}H_{14}$ can exist in four isomeric forms given below. The isomer that can be identified uniquely by mass spectrometry is which one. Explain your answer : 4

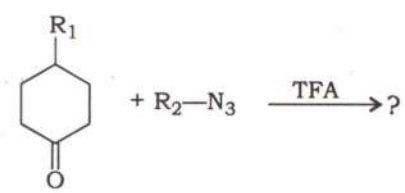


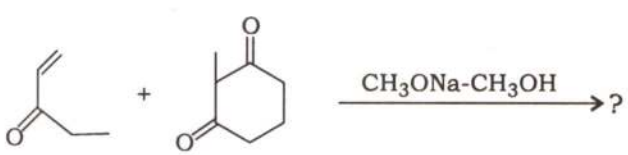
(i) In the PMR (^1H) spectrum recorded at 293 K, an organic compound C_3H_7NO exhibited signals at δ 7·8 (1H, s), 2·8 (3H, s) and 2·6 (3H, s). Identify the structure of the compound and explain your answer. 4

(j) Arrange the following olefins in the correct order of IR stretching frequency of C=C and explain your answer : 4



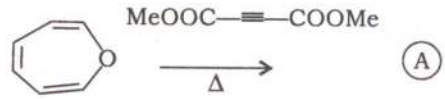
7. (a) Complete the following reactions and sketch a suitable mechanism for these reactions : 5+5=10

(i) 

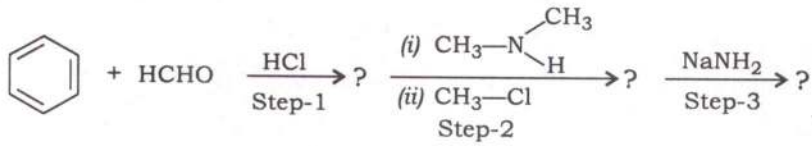
(ii) 

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(b) Explain the type of ring closure and the major product (A) formed in the following reaction : 5

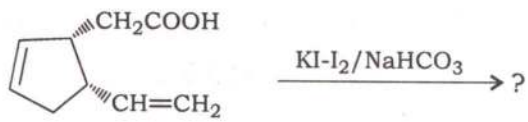


(c) Complete the following reactions and give the mechanism for the conversion of the step-2 product into the step-3 product : 5

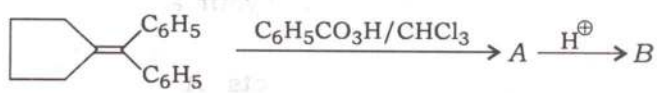


(d) Complete the following reactions and give the appropriate mechanisms : 5+5=10

(i)



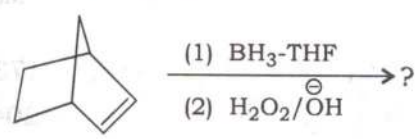
(ii)



8. (a) (i) Complete the following reaction and explain the mechanism involved :



(ii) Complete the following reaction and provide suitable mechanism and stereochemistry of the product :



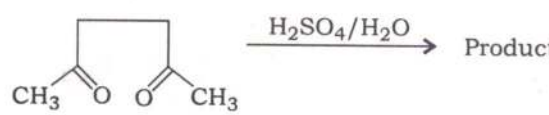
5+5=10

(b) Write the photochemical irradiation products of the following compounds : 5

(i) 2-pentanone

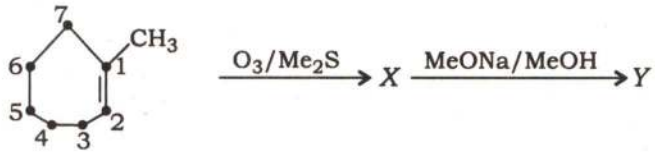
(ii) *trans*-2,6-dimethylcyclohexanone

(c) Predict the product of the following reaction and explain the mechanism involved : 5



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(d) Identify the products X and Y in the following reaction sequence. Explain the mechanism of conversion of X to Y : 10



9. (a) An organic compound having C, H, N and X gave the following spectral data :

UV : λ_{max} : 240 (ε 8000), 300 (ε 100) nm

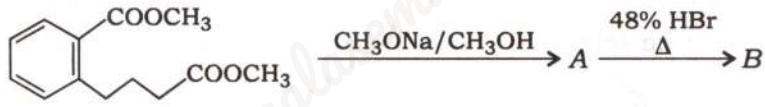
IR : ν_{max} KBr : 3400, 3300, 3200 (w), 2900, 1620, 1600, 1500, 1380, 880, 820 cm^{-1}

^1H NMR : δ 7·20 (1H, d, $J = 9$ Hz), 6·50 (1H, d, $J = 3·5$ Hz), 6·30 (1H, dd, $J = 9$ Hz and 3·5 Hz), 3·50 (2H, broad s, removed on adding D_2O), 2·30 (3H, s)

Mass : m/z (RA) : 187 (90), 185 (90), 186 (20), 184 (20), 160 (10), 158 (10), 106 (100)

Find the structure of the compound and justify your answer. 10

(b) In the following reactions, identify the products A and B. Explain the mechanism of formation of A : 5



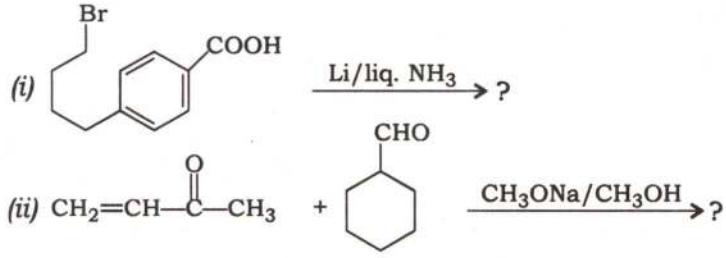
(c) (i) What is the concentration value for a solution of camphor ($\varepsilon_{max} = 14$) in hexane solution in a 10 cm cell? A at 295 nm was found to be 2·52.

(ii) Offer your explanation for the variation of λ_{max} values for the following compounds :

Methyl chloride	$\lambda_{max} = 173$ nm
Methyl bromide	$\lambda_{max} = 204$ nm
Methyl iodide	$\lambda_{max} = 258$ nm

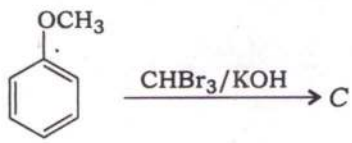
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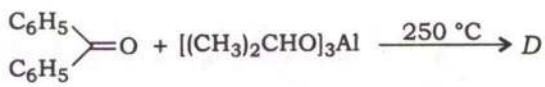
(d) Formulate the products and mechanisms of the following reactions : 5+5=10



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10. *(a)* Predict the products *C* and *D* in the given reaction scheme [*(i)* and *(ii)*]. Provide the suitable mechanisms for both the reactions : 5+5=10

(i) 

(ii) 

(b) Find the structure of the organic compound with molecular formula $C_{15}H_{14}O$ which exhibited the following ^1H NMR and ^{13}C NMR spectral data. Justify your answer : 5

^1H NMR : δ 2·4 (s), 7·2 (d, J = 8 Hz), 7·7 (d, J = 8 Hz)

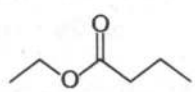
^{13}C NMR : δ 21·0, 129·0, 130·0, 136·0, 141·0, 190·0

(c) Explain the following : 5

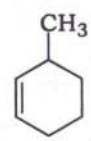
(i) *p*-nitroaniline and anthracene both absorb near 375 nm but *p*-nitroaniline is yellow while anthracene is colourless.

(ii) Monomeric saturated aliphatic carboxylic acids show carbonyl stretching frequency near 1760 cm^{-1} while the saturated aliphatic ketones near 1720 cm^{-1}.

(d) *(i)* Explain the mass spectral fragmentation of the following compounds *A* and *B* :



A



B

(ii) An unknown organic compound with molecular formula $C_{10}H_9NO_2$ gives the following spectral data :

IR : 2210, 1724 cm^{-1}

^1H NMR : δ 1·4 (t, J = 7·1 Hz, 3H), 4·4 (q, J = 7·1 Hz, 2H),
7·7 (d, J = 7·0 Hz, 2H), 8·2 (d, J = 7·0 Hz, 2H)

^{13}C NMR : δ 16, 62, 118, 119, 125, 126, 127, 168

Identify the structure and justify your answer. 10

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