



**WEST BENGAL STATE UNIVERSITY**

B.Sc. Honours Part-II Examination, 2022

**CHEMISTRY**

**PAPER: CEMA-III**

Time Allotted: 4 Hours

Full Marks: 100

*The figures in the margin indicate full marks.  
Candidates should answer in their own words and adhere to the word limit as practicable.  
All symbols are of usual significance.*

**GROUP-A**

**CEMAT-23-IA**

**Answer any two questions taking one from each Unit**

**Unit-I**

1. (a) Account for the anomalous behaviour of the ionisation energies ( $\text{kJ mol}^{-1}$ ) of Group 13 elements as given below: 3
- |     |     |     |     |     |
|-----|-----|-----|-----|-----|
| B   | Al  | Ga  | In  | Tl  |
| 800 | 577 | 579 | 558 | 589 |
- (b) Discuss the variation in properties of Group 14 elements with reference to 2+2+2  
(i) Oxidation state (ii) Electronegativity (iii) Metallic character
- (c) (i) Explain why  $\text{BCl}_3$  is mono-meric but  $\text{AlCl}_3$  is a dimer. 2+2  
(ii)  $\text{SiCl}_4$  is hydrolysed easily whereas  $\text{CCl}_4$  is resistant to hydrolysis — Justify.
2. (a) Write the structure of Thiosulfuric and Disulfuric acids and mention the oxidation state of Sulphur atoms in each compound. Discuss the hybridisation of central Sulphur for each case. 4
- (b) Why does iodine show evidences of electropositive character? Cite two examples which prove the existence of electropositive iodine. 1+2
- (c) What happens when  $\text{NaNH}_2$  is treated with  $\text{N}_2\text{O}$ ? 2
- (d)  $\text{PCl}_3$  and  $\text{NCl}_3$  hydrolyse in different mode — Explain giving equations. 2
- (e) Explain with reasons why  $\text{SF}_6$  is known but not  $\text{SCl}_6$ . 2

**Unit-II**

3. (a) Draw the qualitative M.O. energy level diagram of  $\text{CN}^-$ . Can  $\text{CN}^-$  act as an ambidentate ligand? Discuss in the light of M.O. theory. 3+2

- (b) What do you mean by coordination position isomerism? Give an example to illustrate the definition. 1+1
- (c) The fifth water molecule in  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  is lost at a higher temperature than the other four molecules. Explain the observation. 2
- (d)  $[\text{Cr}(\text{en})_2\text{Cl}_2]\text{Cl}$  is found in two forms, one violet and other green. On reaction with oxalate ion, the violet species produces corresponding oxalato derivative, while the green does not. Explain the result and write the IUPAC name of the oxalato derivative. 2+1
4. (a) Discuss the stereo-isomerism of co-ordination complexes having co-ordination number 4 with examples. 3
- (b) Draw the qualitative M.D. energy level diagram of CO and calculate the bond order. 2+1
- (c) What is the characteristic of semiconductors? Give one example. What is the basic difference between semiconductors and superconductors? 3
- (d) State and explain two factors which determine  $\text{N}^-$  or  $\text{O}^-$  coordination of  $\text{NO}_2^-$ . 3

**CEMAT 23-IB**

**Answer any two questions taking one from each Unit**

**Unit-I**

5. (a) How does structure of boron nitride differ from that of graphite? 2
- (b) The product of the reactions of diborane with ammonia depends on conditions of the experiment. — Explain with examples. 3
- (c) Hydroxylamine can function both as oxidising and reducing agent. Explain and give appropriate examples. 1+2
- (d) What are freons? Explain the effect of photolytic reactions of freons in the upper atmosphere. 1+2
- (e) What happens when borazine is treated with HCl? Give equation. 2
6. (a) Give the method for preparation of straight chain and cross-linked silicones. Discuss how the uses of silicones are linked to their properties. 1+3
- (b) Complete the following equations: 3
- (i)  $\text{XeF}_2 + \text{SO}_3 \rightarrow$       (ii)  $\text{XeF}_2 + \text{NO} \rightarrow$       (iii)  $\text{XeF}_4 + \text{H}_2\text{O} \xrightarrow{-80^\circ \text{C}}$
- (c) Discuss the structure and bonding of  $\text{ClF}_3$ . 3
- (d) What are  $\text{NO}_x$ ? Discuss the role of freons in ozone layer depletion. 1+2

**Unit-II**

7. (a) Explain the significance of the principle of solubility product and common ion effect for the precipitation of iron, aluminum and chromium as hydroxides in qualitative analysis. 3

- (b) Calculate the cell potential ( $E_{\text{cell}}$ ) for the cell containing 0.1 (M)  $\text{Ag}^+$  and 4.0 (M)  $\text{Cu}^{2+}$  at  $25^\circ\text{C}$ . ( $E^0_{\text{Cu}^{2+}/\text{Cu}} = 0.34\text{V}$  ;  $E^0_{\text{Ag}^+/\text{Ag}} = 0.80\text{V}$ ). 3
- (c) What is Ellingham diagram? How can the thermodynamics of metallurgical processes be predicted from Ellingham diagram? 3
- (d)  $\text{Mn}^{2+}(\text{aq.})$  is oxidised to  $\text{MnO}_4^-$  by sodium bismuthate in dil.  $\text{HNO}_3$  medium. Balance the reaction by ion-electron method. 3
8. (a) Distinguish between disproportionation and comproportionation reactions. Explain why  $\text{Cu(I)}$  is not stable in aqueous solution. 2+1
- $[E^0_{\text{Cu}^{2+}/\text{Cu}^+} = +0.15\text{V}, E^0_{\text{Cu}^{2+}/\text{Cu}} = +0.34\text{V}]$
- (b) Calculate the  $\text{S}^{2-}$  ion concentration in a 0.25 (M)  $\text{HCl}$  solution saturated with  $\text{H}_2\text{S}$  at  $25^\circ\text{C}$  from the following data: 3+1
- (i) Concentration of the saturated solution of  $\text{H}_2\text{S}$  at  $25^\circ\text{C}$  is 0.1(M)
- (ii) The primary and secondary dissociation constants of  $\text{H}_2\text{S}$  are  $9.1 \times 10^{-8}$  and  $1.2 \times 10^{-15}$  respectively.
- Hence, calculate the maximum concentration of  $\text{Cd}^{2+}$  which will remain in solution after precipitation as  $\text{CdS}$  under these conditions.
- $[K_{\text{sp}}(\text{cds}) = 5.5 \times 10^{-25} \text{ g ion}^2/\text{L}^2]$
- (c)  $E^0_{\text{MnO}_4^-/\text{Mn}^{2+}} = 1.51\text{V}$  and  $E^0_{\text{Cr}_2\text{O}_7^{2-}/2\text{Cr}^{3+}} = 1.33\text{V}$ . Calculate the pH at which these two couples will have the same reduction potential. 3
- (d) The solubility product of ferric hydroxide is  $1.1 \times 10^{36}$  at  $25^\circ\text{C}$ . Calculate solubility of ferric hydroxide in g / L at this temperature. 2

### GROUP-B

#### CEMAT-23-OA

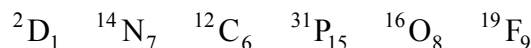
Answer any *two* questions taking *one* from each unit

#### Unit-I

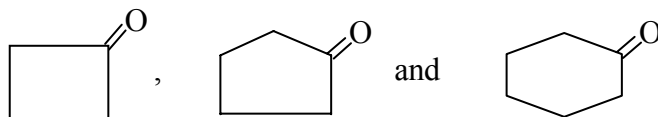
9. (a) How would you distinguish between the members in the following pairs of compound? 2×3
- (i) N,N,2,6-tetramethylaniline and N,N,3,5-tetramethylaniline by UV spectroscopy.
- (ii) Di-*tert*-butylketone and diethylketone by  $^1\text{H-NMR}$  spectroscopy.
- (iii) Acetylacetone and acetone by IR spectroscopy.
- (b) An organic compound ( $\text{C}_{10}\text{H}_{12}\text{O}_2$ ) has the following spectral data: 4
- IR ( $\text{cm}^{-1}$ ): 3050, 2950, 1730.
- $^1\text{H-NMR}$  (in ppm):  $\delta$  1.30(6H, d); 5.20(1H, m); 7.20(3H, m); 8.00 (2H, m).
- Deduce the structure of the compound with the justification of the spectral data.

- (c) Explain why acetic anhydride shows two carbonyl stretching frequencies in IR spectroscopy? 1½
- (d) In <sup>1</sup>H-NMR spectroscopy, a particular proton appears at 402 Hz downfield from TMS in a 180 MHz instrument. Calculate its δ-value. 1½

10.(a) Which of the following nuclei are NMR active — Justify. 3



(b) Arrange the following cyclic ketones in increasing order of their carbonyl stretching frequency. Give reason for your answer. 2



(c) An organic compound with molecular formula C<sub>3</sub>H<sub>5</sub>OCl evolves CO<sub>2</sub> when added to aqueous NaHCO<sub>3</sub> solution. Its IR absorption shows a band at 1795 cm<sup>-1</sup>. It gives a triplet and a quartet signals in its <sup>1</sup>H-NMR spectrum. Identify the compound. 3

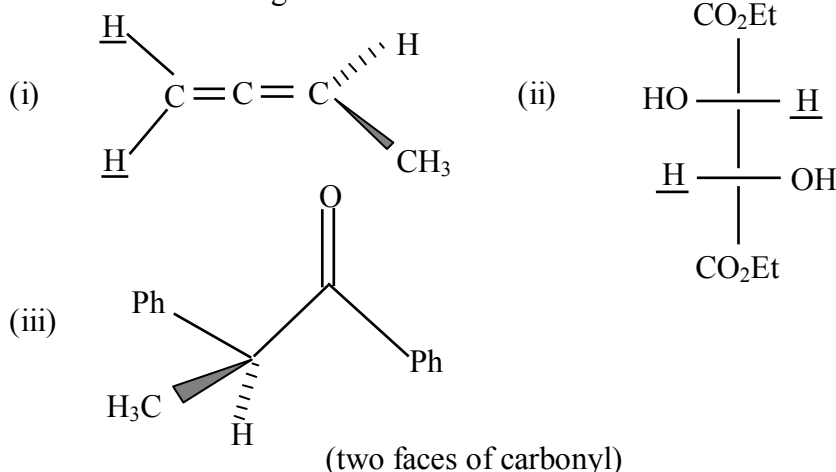
(d) What is metastable peak in mass spectra? Explain with a suitable example. 2

(e) Explain the following: 1½ + 1½

- (i) C = C stretching frequency of cyclobutene appears at 1566 cm<sup>-1</sup>, but that of 1-methylcyclobutene at 1641 cm<sup>-1</sup>.
- (ii) UV spectra of aniline and phenol are pH-dependent.

### Unit-II

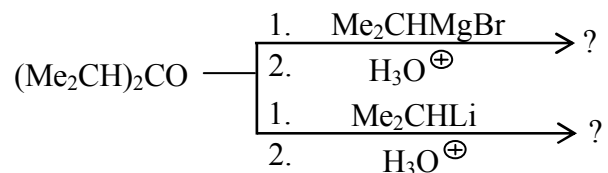
11.(a) Find out the topic relationship between the underlined H atoms and the mentioned faces in the following: 1×3



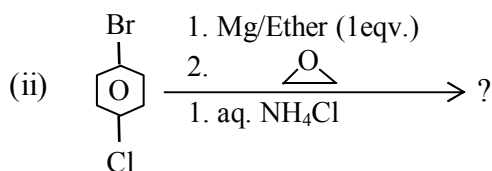
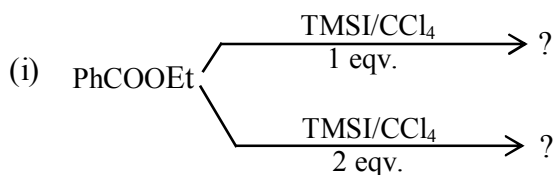
Describe the process by which the relationships are determined.

- (b) Explain what happens when ethyl acetoacetate is separately treated as follows: 3
- (i) Treated with CH<sub>3</sub>COCl and Mg;
- (ii) First sodium salt of ethyl acetoacetate is formed and then treated with acetyl chloride.

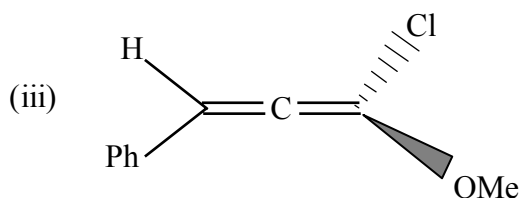
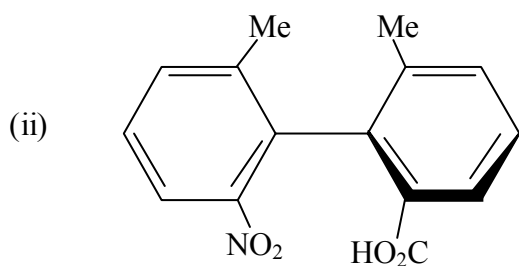
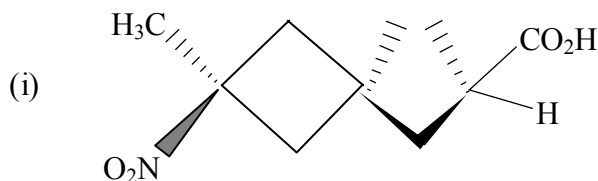
- (c) Carry out the following transformations (any *two*): 2×2
- (i) Phenol to coumarin,
  - (ii) Hydroquinone to 1, 2, 4-trihydroxybenzene,
  - (iii) Phenol to *m*-nitrophenol.
- (d) Complete the following reactions and justify the formation of product in each case. 2



- 12.(a) Explain the formation of the products in the following reactions. 2×2



- (b) Assign R/S-configuration of the following compounds (any *two*): 1 ½ × 2



Mention the relative priorities of different groups in each case.

- (c) Fries rearrangement may be either inter- or intramolecular in nature. Give evidence in favour of the fact. 2

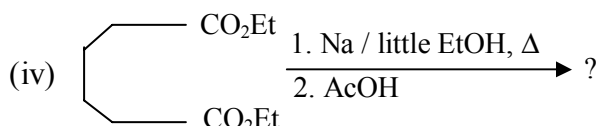
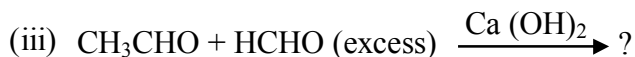
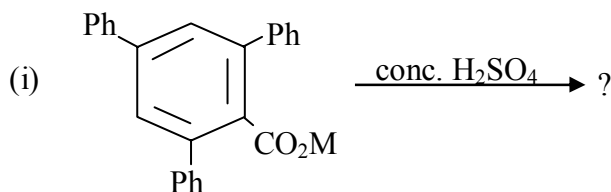
- (d) A given sample of optically active 2-butanol shows the specific rotation of  $-6.76^\circ$ . If pure (+)-2-butanol has the specific rotation of  $+13.52^\circ$ , what is the molar ratio of two enantiomers in the given sample? 3

## CEMAT-23-OB

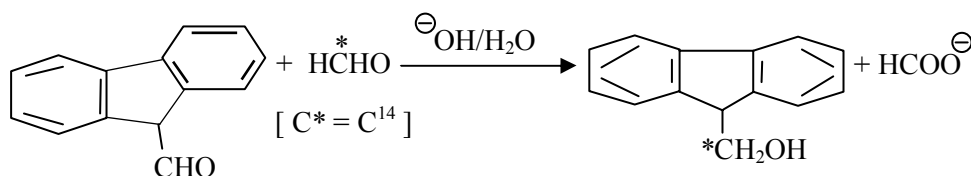
Answer any *two* questions taking *one* from each unit.

## Unit-I

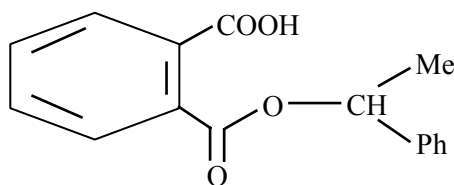
- 13.(a) Complete the following reactions giving mechanism (any *three*): 3×3



- (b) Both *p*-dimethylaminobenzaldehyde and *p*-nitrobenzaldehyde fail to undergo benzoin condensation but the mixture of these two undergoes the same condensation. Give the product with the explanation of its formation. 2
- (c) Write down the mechanism of the following reaction. 2



- 14.(a) Alkaline hydrolysis of the optically active half ester given below, forms the racemic alcohol  $\text{Ph}(\text{Me})\text{CHOH}$ . Explain with mechanism. 3

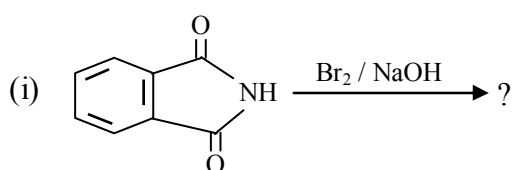


- (b) How do you convert  $\text{PhCOCH}_3$  to mandelic acid? Show the steps giving reagents and reaction conditions. 2
- (c) Show the steps for the conversion of  $\text{PhCHO}$  to  $\text{PhCDO}$ . 2
- (d) Arrange the following compounds in decreasing order of their rates of hydrolysis in alkaline medium and justify your answer. 2
- (i)  $\text{CH}_3\text{COCl}$       (ii)  $\text{CH}_3\text{CONH}_2$       (iii)  $\text{CH}_3\text{COOC}_2\text{H}_5$

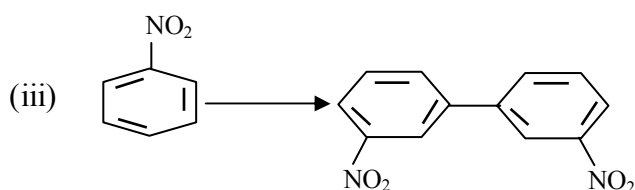
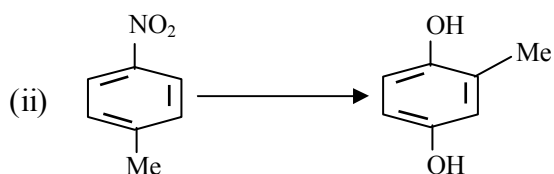
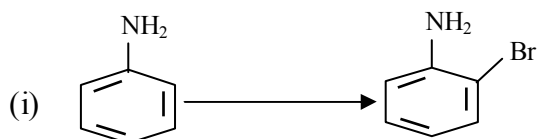
- (e) In the Perkin reaction of PhCHO with Ac<sub>2</sub>O and NaOAc, little styrene is obtained. — Explain. 2
- (f) What happens when racemic lactic acid is heated? 2

**Unit-II**

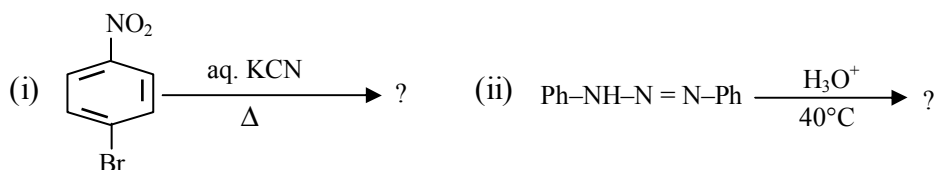
- 15.(a) State the action of NaNO<sub>2</sub> / HCl on: 3
- (i) N-methylaniline (ii) N, N-dimethylaniline and (iii) Benzylamine
- (b) How do you chemically distinguish between C<sub>2</sub>H<sub>5</sub>CN and C<sub>2</sub>H<sub>5</sub>NC? 2
- (c) Predict the products with plausible mechanism in the following reactions: 3



- (d) Carry out the following transformations (any *two*): 2×2



- 16.(a) Give the product (s) formed in the following reactions giving plausible mechanisms. 2×2

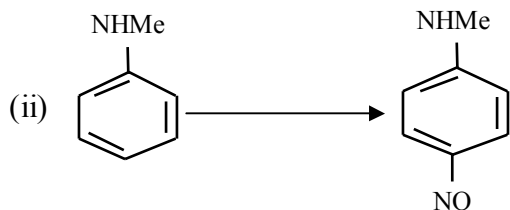
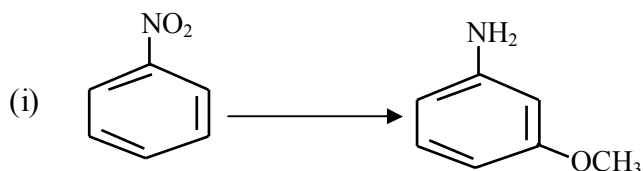


- (b) Give an example of each of the following: 1+1

- (i) Diazomethane acts as a 1, 3-dipolar reagent.
- (ii) Diazomethane acts as a base.

(c) Carry out the following conversions.

2×2



(d) Predict the product in the following reaction. Give the probable mechanism.

2



**N.B. :** Students have to complete submission of their Answer Scripts through E-mail / Whatsapp to their own respective colleges on the same day / date of examination within 1 hour after end of exam. University / College authorities will not be held responsible for wrong submission (at in proper address). Students are strongly advised not to submit multiple copies of the same answer script.

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