

West Bengal State University
B.A./B.Sc./B.Com. (Honours, Major, General) Examinations, 2014
PART-II
CHEMISTRY- Honours
Paper- III
(New and Old Syllabus)

Duration : 4 Hours

Full Marks : 100

Candidates are required to give their answers in their own words as far as practicable.

The figures in the margin indicate full marks.

(New Syllabus)

Use separate answer scripts for [**CEMAT-23-IA & CEMAT-23-IB**]

Group - A

(Inorganic Chemistry)

CEMAT-23-IA

Answer *four* questions, taking *one* from each Unit.

UNIT - I

1. a) How does the acidity of the oxy-acids of chlorine varies with oxidation state ? Discuss with reason. 3
- b) Elemental nitrogen exists as the gaseous dinitrogen molecule while elemental phosphorous forms solid P_4 molecule. Explain. 2 + 2
- c) What happens when —
- (i) SO_2 is passed into an aqueous suspension of pyrolusite. 2 + 2
- (ii) $NaNH_2$ is treated with N_2O . 2 + 2
- d) How is NH_2OH prepared ? Give one example of its oxidising property. 1 + 1

2. a) Justify : BF_3 exists as monomeric state whereas BH_3 as dimeric state. 2
 b) What happens when NaClO_3 is allowed to react with oxalic acid at 90°C ? 2
 c) H_3BO_3 acts as a strong monobasic acid in presence of glycerol. Explain. 2
 d) Between H_2SO_4 and H_2SeO_4 which one is stronger oxidising agent ? Give reasons. 3
 e) The mode of hydrolysis of PCl_3 and NCl_3 are different. Explain with equations. 2
 f) H_2SiF_6 is a stable compound but H_2SiCl_6 is non-existent. Explain. 2

Unit - II

3. a) Write down the molecular orbital diagram for CO and explain why it acts as a σ -donor involving C rather than O. 3 + 1
 b) (i) PH_3 is more volatile than NH_3 . Explain. 2
 (ii) O_2^+ and N_2^+ have almost the same bond lengths. Explain. 2
 (iii) Find out the total number of bonding, non-bonding and anti-bonding electrons in HF. 2
 c) Give the IUPAC names of the following compounds. 1 + 1
 (i) $\text{K} [\text{Ag}(\text{CN})_2]$
 (ii) $[\text{Co}(\text{en})_3] [\text{Co}(\text{OX})_3]$ [where en = ethylene diamine and OX = Oxalate (2 -) ion].
4. a) Give the MO diagram of O_2 molecule. Now state which of the following species will be paramagnetic :
 (i) O_2^+ (ii) O_2 (iii) O_2^- (iv) O_2^{2-} . 2 + 1
 b) Arrange the stability order of the following : 2
 NO , NO^+ , NO^-
 c) How will you distinguish between —
 (i) $[\text{Co}(\text{NH}_3)_5\text{Br}] \text{SO}_4$ and $[\text{Co}(\text{NH}_3)_5\text{SO}_4] \text{Br}$
 (ii) *cis*- $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$ and *trans*- $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$ 2 + 2
 d) What are intrinsic semiconductors ? How *n*- and *p*-type semiconductors can be prepared by doping ? 1 + 2

CEMAT-23-IB

Answer two (2) questions taking one from each unit.

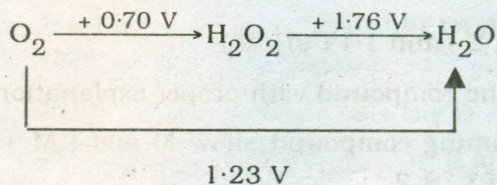
Unit - I

5. a) Explain the following :
- (i) Four B — H bonds in B_2H_6 are shorter than the other two B — H bonds. 2 + 2
- (ii) $B_3N_3H_6$ is more reactive than C_6H_6 . 1 + 1 + 1
- b) Hydrazine can exhibit both oxidizing and reducing property — Justify this statement with suitable example. 3 × 2 = 6
- c) What happens when —
- (i) An aqueous solution of NaN_3 is treated with acidified $KMnO_4$.
- (ii) Iodine-azide solution is treated with trace amount of $Na_2S_2O_3$.
- (iii) XeF_2 is treated with HCl.
6. a) Discuss the structure and bonding of ClF_3 molecule. 3
- b) What happens when —
- (i) Hydroxylamine is allowed to react with $Fe(OH)_2$.
- (ii) Sodium thiosulphate is allowed to react with iodine solution. 2 × 2
- c) How is XeF_6 prepared ? Discuss its structure. 1 + 2
- d) What are freons ? Discuss their roles in the ozone layer depletion. 1 + 2

UNIT-II

7. a) Find out the equivalence point potential for the titration of Fe^{2+} with MnO_4^- at pH = 0. Given $E^\circ(MnO_4^-, H^+/Mn^{2+}) = +1.52 V$
- $$E^\circ(Fe^{3+}/Fe^{2+}) = +0.77 V. \quad 3$$
- b) Establish the Nernst equation for the couple VO_3^-/VO^{2+} . E° value for the couple is 0.92 V at 25°C in 1M acid medium. Find its formal potential at pH = 7. 3
- c) From the Latimer diagram
- $$Ag^{+2} \xrightarrow{+1.98 V} Ag^+ \xrightarrow{+0.80 V} Ag$$
- Find out $E^\circ(Ag^{+2}/Ag)^\circ$. 1

- d) Explain the role of phosphoric acid in the titration of Fe^{2+} with $\text{Cr}_2\text{O}_7^{2-}$ in acid medium with BDS as the indicator. 2
- e) The potential for $\text{Fe}^{3+}/\text{Fe}^{2+}$ and Fe^{2+}/Fe couples are + 0.77 V and - 0.41 V respectively. Ascertain whether Fe^{2+} will disproportionate to Fe^{3+} and Fe. 3
8. a) Construct the Frost diagram of oxygen from the Latimer diagram given below and show the calculation for evaluation of the position of each point of the plot. 3



- b) The overall formation constant of $[\text{Fe}(\text{CN})_6]^{4-}$ ion is 10^{35} and E° value for $\text{Fe}^{3+}/\text{Fe}^{2+}$ and $[\text{Fe}(\text{CN})_6]^{3-}/[\text{Fe}(\text{CN})_6]^{4-}$ couples are + 0.77 V and + 0.36 V respectively. Calculate the overall formation constant of $[\text{Fe}(\text{CN})_6]^{3-}$ ion. 3
- c) What is common ion effect? Why is NH_4Cl added before the addition of NH_4OH for the precipitation of Gr.IIIA cations during group analysis. 1 + 2
- d) $E^\circ_{\text{Cu}^{2+}/\text{Cu}^+} = 0.15 \text{ V}$. $E^\circ_{\frac{1}{2}\text{I}_2/\text{I}^-} = 0.54 \text{ V}$. So according to the E° values I^- should not be oxidized to I_2 but in actuality it is oxidized. Explain. 3

Use separate answer scripts for [CEMAT-23-OA & CEMAT-23-OB]

Group - B

(Organic Chemistry)

CEMAT-23-OA

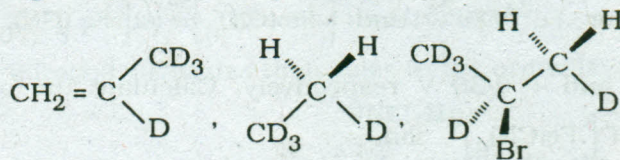
Answer two (2) questions taking one from each unit.

UNIT - I

9. a) An organic compound with molecular formula $C_6H_{12}O$ gives positive iodoform test. Its UV, IR and 1H NMR data are given below :
- UV : λ_{max} 282 nm, ϵ_{max} 22
- IR : ν_{max} 1710 cm^{-1}
- 1H NMR : δ (2.1) (3 H, S) and 1.1 (9H, S)

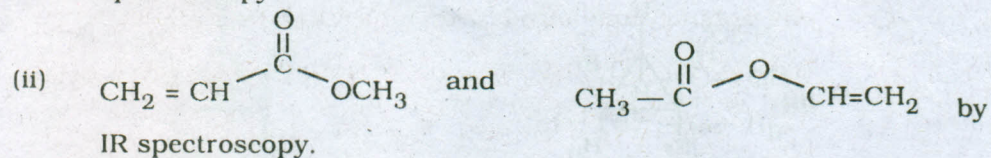
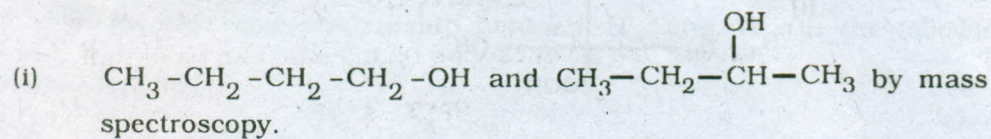
Deduce the structure of the compound with proper explanation. 3

- b) Why does bromine containing compound show M and (M + 2) peaks with a relative intensity of 1 : 1 ? 1
- c) Label the different types of magnetically non-equivalent hydrogens of the following compounds and justify your answer : 3

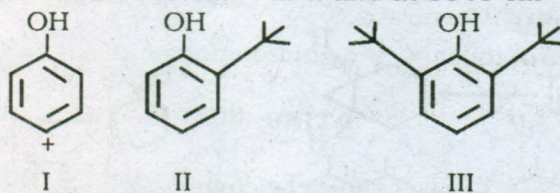


- d) Predict and explain the changes in the auxochromic red shifts in (i) acidifying $C_6H_5NH_2$ and (ii) basifying C_6H_5OH . 2
- e) Which of the following is/are not NMR active ? 1
- ^{12}C , 2H , ^{19}F .
- f) Explain the following : 1 + 2
- Ethylene fails to show any IR signal around 1600 cm^{-1} .
 - Acetylenic hydrogens resonate at higher field (upfield) than vinylic hydrogens.

10. a) Draw the ^1H NMR signals of $\text{CH}_3\text{-CH}_2\text{-Br}$ showing the relative chemical shifts, integration and spin-spin coupling patterns. 3
- b) Distinguish between the compounds in each of the following pairs by the methods as directed. 2×2

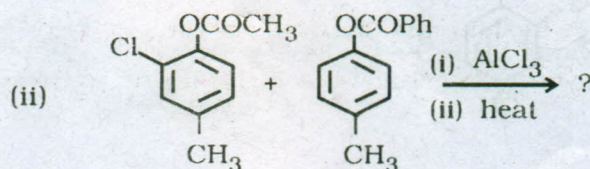
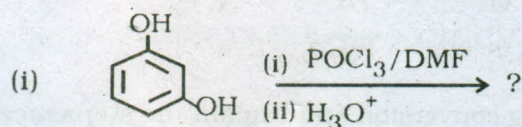


- c) 'In case of α, β -unsaturated carbonyls, the R-bands (the $n \rightarrow \pi^*$ transition) show a blue shift on increasing the polarity of the solvent in their UV spectra'. Explain. 3
- d) In the substituted phenols the O — H stretching is at 3608 cm^{-1} in I, at 3605 cm^{-1} and 3643 cm^{-1} in II and at 3643 cm^{-1} in III. Explain. 3

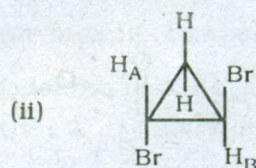
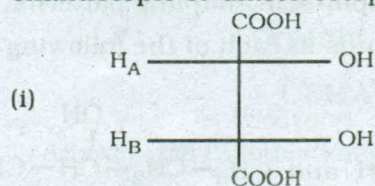


UNIT - II

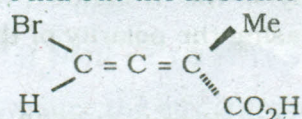
11. a) Predict the products with plausible mechanism : $2 \frac{1}{2} + 2 \frac{1}{2}$



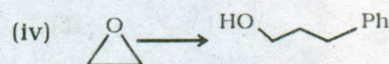
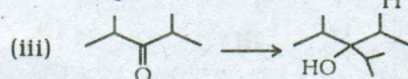
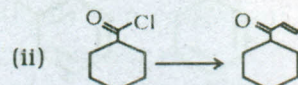
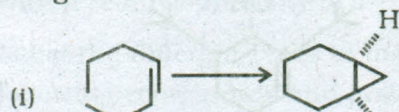
- b) Identify H_A and H_B in each of the following structures as homotopic, enantiotopic or diastereotopic. 1 + 1



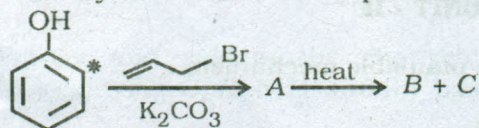
- c) Find out the absolute (R/S) configuration of the following compound :



- d) Carry out the following conversion using suitable organometallic reagents. 4

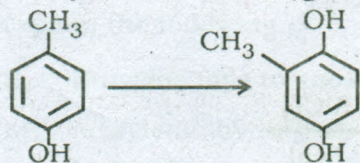


12. a) Identify A, B and C and explain their formation :



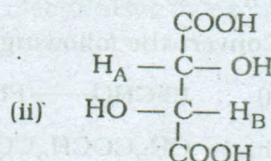
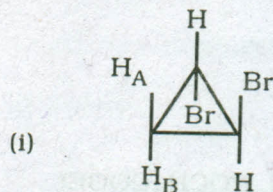
$C^* = \text{C}^{14}$ dry acetone. 3

- b) Carry out the following conversion and explain the steps mechanistically.



3

- c) Give the Fisher formula of the compound formed by replacement of Pro-S hydrogen of ethanol with a — COOH group. What is the configuration at the new stereogenic centre ? 2
- d) Indicate the topic relationship between H_A and H_B in the following compounds. 2



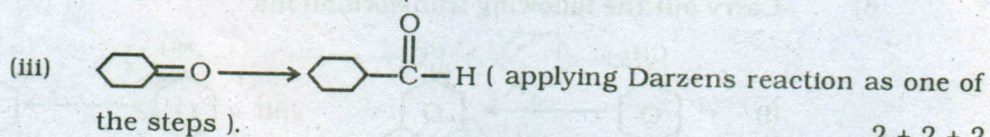
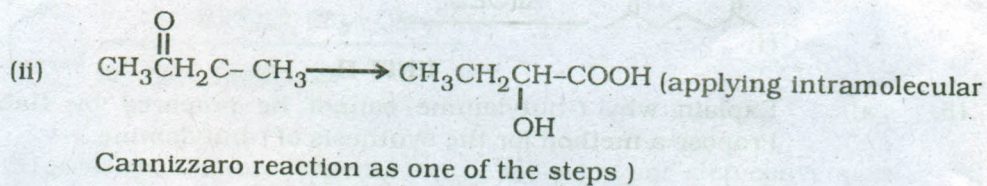
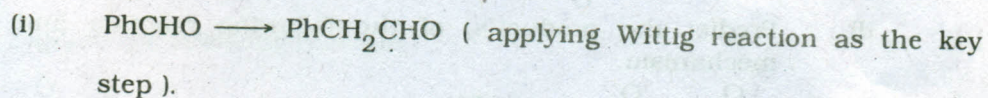
- e) Synthesise $\text{PhCH} = \text{C}(\text{Et})\text{COOH}$ using Reformatsky reaction. Why magnesium metal cannot be used in place of Zn ? 2

CEMAT 23-OB

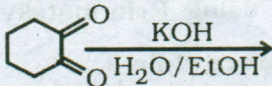
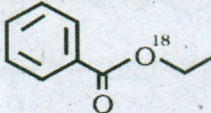
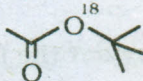
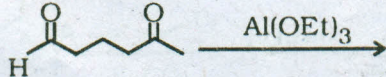
Attempt any *two* questions taking *one* question from each Unit.

UNIT-I

13. a) Carry out the following conversions :

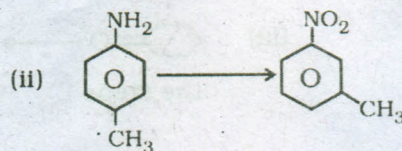
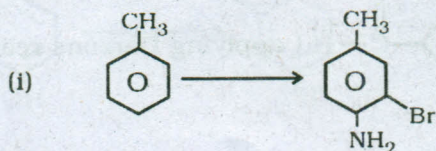


2 + 2 + 2

- b) When the benzoin $\text{Ar}^1\text{CHOHCOAr}^2$ is heated with an aldehyde Ar^2CHO in the presence of KCN, a mixed benzoin $\text{Ar}^2\text{CHOHCOAr}^1$ is obtained. Explain. 3
- c) Identify the products (A), (B), (C) in the following conversion :
 $\text{PhCHO} \xrightarrow[\text{NaOEt}]{\text{MeNO}_2} (\text{A}) \xrightarrow{\text{LiAlH}_4} (\text{B}) \xrightarrow{\text{HNO}_2} (\text{C})$ 2
- d) Identify the product with plausible mechanism.
 $\text{Ph}_3\text{CCO}_2\text{H} + \text{MeOH} \xrightarrow{\text{conc. H}_2\text{SO}_4} ?$ 2
14. a) Convert the following : 2 + 2
- (i) $\text{PhCHO} \longrightarrow \text{PhCDO}$
- (ii) $\text{CH}_3\text{COCH}_2\text{COOEt} \longrightarrow \text{CH}_3\text{CH}_2\text{COCH}_2\text{COOEt}$
- b) Predict the product(s) of the following reaction and give mechanism. 2
- 
- c) Explain the mechanism of alkaline hydrolysis of the following O^{18} labelled esters in ordinary water (H_2O^{16}) and indicate the distribution of O^{18} in the products in each case. 2 x 2
- (i)  (ii) 
- d) Predict the product(s) of the following reaction and give plausible mechanism. 3
- 

UNIT-II

15. a) Explain why *t*-butylamine cannot be prepared by Gabriel synthesis. Propose a method for the synthesis of *t*-butylamine. 3
- b) Carry out the following transformations : $2 \frac{1}{2} + 2 \frac{1}{2}$



(Old Syllabus)

Duration : 4 Hours

Full Marks : 100

Candidates are required to give their answers in their own words as far as practicable.

The figures in the margin indicate full marks.

Use separate answer scripts for Group A and Group B.

Group-A**(Inorganic Chemistry)**

(Full Marks - 50)

Answer any *three* questions, taking *one* from each Unit.

UNIT - I

1. a) What do you mean by radius ratio in ionic crystal? What information can be obtained from it? Derive the limiting value of radius ratio in tetrahedral coordination. 1 + 2 + 3
- b) Arrive at the shapes of XeO_2F_2 and ClF_3 using VSEPR method. Show the electron count. 2 + 2
- c) Give examples of the following types of ligand : 2
- (i) σ -donor and π -acceptor
- (ii) only σ -donor.
- d) What are the possible geometrical isomers of the following complexes? 2
- (i) $[\text{Ru}(\text{Py})_3(\text{Cl})_3]$
- (ii) $[\text{CO}(\text{en})_2(\text{NO}_2)\text{Cl}]^+$
- e) Explain the effect on conducting properties of silicon on doping with arsenic. 4

2. a) What is meant by lattice energy of an ionic solid ? Construct Born-Haber cycle for the formation of KCl crystal starting from solid potassium metal and gaseous chlorine. Calculate the lattice energy of crystalline KCl using the following data : 1 + 2 + 3

Sublimation energy of $K(s) = + 89 \text{ kJ mole}^{-1}$

Bond dissociation energy of $Cl_2(g) = +244 \text{ kJmol}^{-1}$

Ionisation energy of $K(g) = + 425 \text{ kJmol}^{-1}$

Electron affinity of $Cl(g) = - 355 \text{ kJ mol}^{-1}$

Heat of formation of $KCl(s) = - 438 \text{ kJ mol}^{-1}$.

- b) HgI_2 is much less soluble in water than $HgCl_2$. Explain. 2
- c) Draw the MO energy level diagram for NO molecule. Compare the bond dissociation energies of NO^+ and NO^- species and explain the difference. 2 + 2
- d) Write IUPAC names of the following :
- (i) $[Cr(NCS)_4(NH_3)_2]^-$
- (ii) $[Ni(CO)_3Py]$ 2
- e) Distinguish between intrinsic and extrinsic semiconductors with example. 4

UNIT-II

3. a) Give a comparative account of the chemistry of Group-15 elements (N, P, As, Sb, Bi) with reference to —
- (i) Oxidation state
- (ii) Oxides and
- (iii) Hydrolytic behaviour of their halides. 3 × 3

- b) Explain why :
- (i) Pb(IV) compounds are powerful oxidising agents.
 - (ii) $\text{H}_2\text{S}_2\text{O}_7$ is a stronger acid than H_2SO_4 . 2 × 2
- c) Discuss the diagonal relationship of lithium and magnesium. 3
4. a) Compare the catenating properties of C, Si and Ge. 2
- b) Explain why NO_2 is more stable than N_2O_3 . 2
- c) Compare and contrast :
- (i) Liquid ammonia solution of sodium metal and aqueous ammonia solution of copper sulphate.
 - (ii) The O — O bond distance in H_2O_2 and O_2F_2 . 2 × 3
- d) Compare the acid strengths of the hydrides of Group - 17 elements. 3
- e) Indicate the feasibility of most common and also the highest oxidation states possible for Cr, Mn and Fe. 3

UNIT-III

5. a) Discuss the preparation and use of any one of the following :
- (i) Lead tetraacetate
 - (ii) Perdisulphuric acid. 3
- b) What are the products of reaction of diborane with ammonia at different temperatures ? 4

- c) Give a short note on hydrazoic acid. 2
- d) Show that hydroxylamine can function both as an oxidising and reducing agent. 3
- e) What happens when AgNO_3 is added to a solution of $\text{Na}_2\text{S}_2\text{O}_3$? 2
- f) Complete the following reactions : 2
- (i) $\text{XeF}_2 + \text{HCl} \longrightarrow$
- (ii) $\text{XeF}_6 + \text{H}_2\text{O} \longrightarrow$
6. a) Why is boron nitride called 'Inorganic graphite'? 2
- b) Write short note on any one of the following : 2
- (i) Phosphazine
- (ii) Borazine.
- c) How is ultrapure silicon prepared? Mention one of its uses. 3
- d) What are pseudohalides? 'Cyanogen is a pseudohalogen.' Justify. 1 + 2
- e) Iodine is more soluble in water in presence of iodide. Explain. 2
- f) Explain the effects of photolytic reactions of freons in the upper atmosphere. 4

Group-B

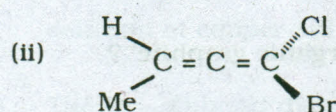
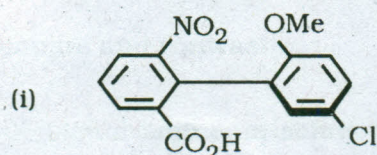
(Organic Chemistry)

[Full Marks - 50]

Answer any three questions, taking one from each Unit.

UNIT - I

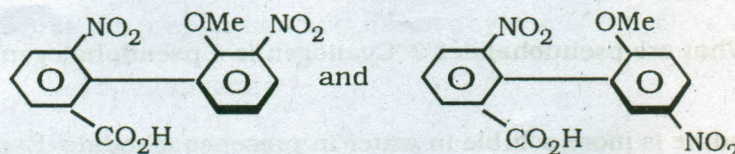
7. a) Assign R/S configurational descriptors to the following molecules : 2



- b) Synthesise phenanthrene from phenylethyl bromide. 2

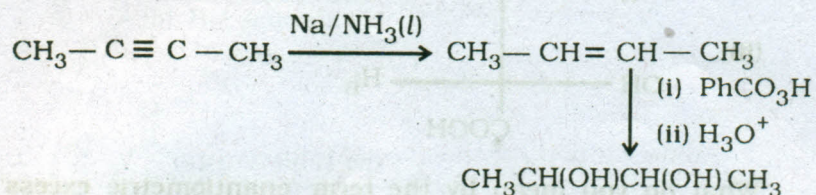
- c) Draw $^1\text{H-NMR}$ signals of $\text{CH}_3\text{CH}_2\text{OH}$ (ordinary grade) showing the relative chemical shifts, integration and spin-spin coupling patterns. 3

- d) Which of the following compounds undergoes racemisation at a faster rate ? Give reasons. 2



- e) How would you distinguish between 4-nitrophenol and 4-nitro-3, 5-dimethyl phenol by UV spectroscopy ? Give relevant explanation. 2

- f) How can you trace the following sequential synthesis by IR spectroscopy? 3



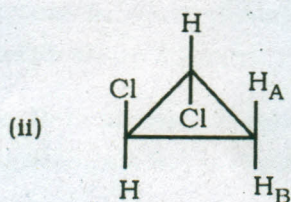
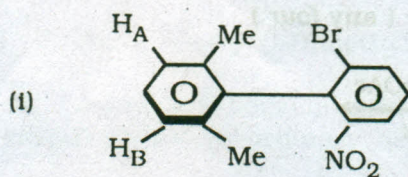
- g) Write the configuration of the product when acetaldehyde is treated with CN^- to the re-face. 2

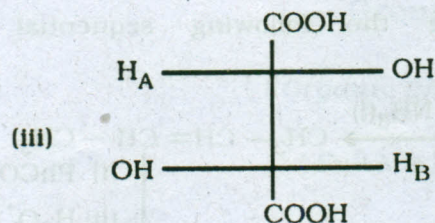
8. a) 9, 10-positions of anthracene are most susceptible to electrophilic attack. Explain. 2

- b) Mesityl oxide shows UV absorption maxima at 230 nm (ϵ 12, 600) and 329 nm (ϵ 41) in hexane and λ_{max} at 243 nm (ϵ 10,000) and λ_{max} 305 nm (ϵ 60) in water. Identify the electronic transitions. Explain why one peak is more intense than other and the absorption maxima are shifted with the change of solvent. 3

- c) How can you resolve (\pm) 2-pentanol? 2

- d) Indicate the topic relationship between H_A and H_B in the following molecules. 3

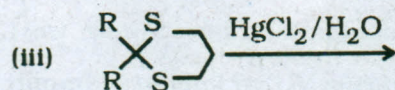
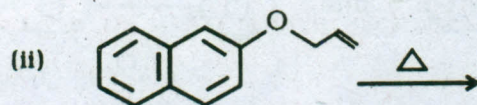
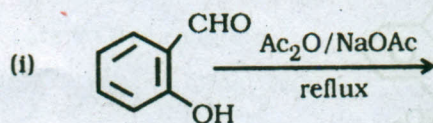


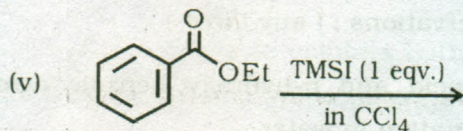
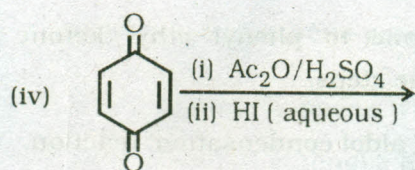


- e) What do you mean by the term 'enantiometric excess' ? The pure (+) enantiomer of a compound shows a specific rotation of $+75^{\circ}\text{C}$. Calculate the percentage of the (-) enantiomer of the same compound in a partially resolved sample showing a specific rotation -30° . 1 + 2
- f) How would you distinguish between the members of the following pairs of compounds ? (any two) : $2 \times 1 \frac{1}{2}$
- (i) δ -lactone and γ -lactone (by IR spectroscopy)
- (ii) *o*-dichlorobenzene and *p*-dichlorobenzene (by PMR)
- (iii) Meso-and dl-butane-2, 3-diol (by IR spectroscopy).

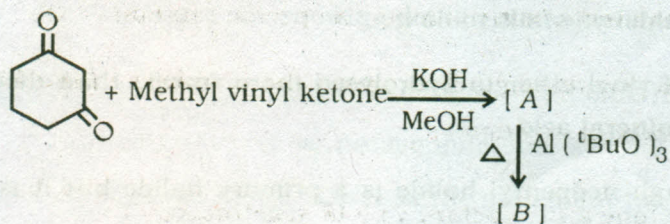
UNIT-II

9. a) Predict the products of the following reactions and give plausible mechanisms in each case : (any four) $2 \times 4 = 8$

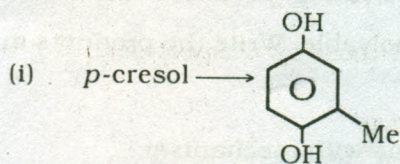




b) Complete the following reaction with explanation. 3



c) Carry out the following transformations : (any two) 2 × 2 = 4



(ii) Benzene \longrightarrow Diphenyl acetic acid

(iii) Acetone \longrightarrow β , β -Dimethyl acrylic acid.

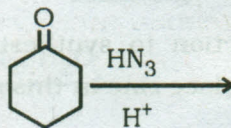
d) 2, 4, 6-trimethyl benzoic acid (mesitoic acid) does not undergo esterification under ordinary acid-catalysed conditions (A_{Ac^2} mode), whereas in concentrated sulphuric acid at 0°C it undergoes quantitative esterification. Explain. 3

10. a) Use Reformatsky reaction to synthesise $PhC(Me) = C(Me)COOH$. Why magnesium cannot replace zinc in this synthesis ? 2 + 1

- b) Convert phenyl methyl ketone to phenyl ethyl ketone by applying Mannich reaction as one of the steps. 2
- c) Give one example of 'Directed aldol condensation' reaction. 1
- d) Explain the following observations : (any three) $3 \times 2 = 6$
- (i) *o*-hydroxy benzoic acid and *p*-hydroxy benzoic acid offer same product upon bromination in water.
- (ii) Chloral usually forms a stable geminal diol whereas trimethyl acetaldehyde fails to do it.
- (iii) Ethyl vinyl ether is hydrolysed more readily than diethyl ether by dil. mineral acid.
- (iv) Though neopentyl halide is a primary halide but it is not used in Wittig reaction.
- e) *dl*- $\text{Me}(\text{CH}_2)_3\text{CH}(\text{OH})\text{COOH}$ on heating, produces two isomeric cyclic compounds of which one is resolvable. Write the products and explain the change. 2
- f) Complete the following reactions with mechanism : 2 + 2
- (i) Resorcinol $\xrightarrow[\text{ZnCl}_2+\text{HCl}]{\text{MeCN}}$
- (ii) $\text{PhCOCHO} \xrightarrow[\text{(ii) H}_3\text{O}^+]{\text{(i) 50\%, NaOH}}$

UNIT-III

11. a) Predict the product in the following reaction and explain :



- b) How is nitromethane prepared from chloroacetic acid ?
- c) Explain what happens when nitromethane is treated with benzaldehyde in presence of ethanolic KOH solution.
- d) Nitrosobenzene exhibits both electrophilic and nucleophilic substitution reactions at *o*- and *p*-position. Explain.
- e) Enlist the common features involved in Hofmann and Lossen rearrangement showing details of the mechanism. $3 + 3 + (2 + 2) + 3 + 3$
12. a) 'Under appropriate condition diazomethane can behave as an electrophile, as a nucleophile, as a 1, 3 dipole or as a source of methylene group.' Discuss the statement taking one suitable example for each.
- b) What happens when *m*-methoxy bromobenzene is treated with NaNH_2 in liq. NH_3 at low temperature ?
- c) Alkaline hydrolysis of benzonitrile affords a salt of benzoic acid but that of 2, 6 dimethyl benzonitrile gives the corresponding amide. Explain with plausible mechanism.
- d) What will be the major product formed when 3-methyl 2-butanone is treated with CF_3COOH . Give the mechanism of the reaction.
- e) Explain the formation of $\text{PhCHOHCH}_2\text{COOEt}$ applying Reformatsky reaction. Why magnesium cannot replace zinc in the above synthesis ?

$4 + 3 + 3 + 3 + 3$
