

West Bengal State University
B.A./B.Sc./B.Com. (Honours, Major, General) Examinations, 2013

PART-II

CHEMISTRY — HONOURS

Paper - III

(NEW & OLD SYLLABUS)

Duration : 4 Hours

[Maximum Marks : 100

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

Marks will be deducted for spelling mistakes, untidiness and bad handwriting.

The figures in the margin indicate full marks.

Use separate answer script for each Group.

(NEW SYLLABUS)

Group - A

(Inorganic Chemistry)

CEMAT 23-IA

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

UNIT - I

1. a) Give a comparative account of the chemistry of group-14 elements (C, Si, Ge, Sn, Pb) with special reference to their
- i) Hydrides (reducing property and thermal stability)
 - ii) Halides (stability in different oxidation states and hydrolytic behaviour).
- 2 + 3
- b) What happens when an acidic solution of I^- and Br^- is treated slowly with excess chlorine water in presence of CCl_4 ? Give balanced equation. 1 + 3
- c) "Hydrazine can exhibit both oxidising and reducing properties." Justify with suitable reactions. 2 + 2

2. a) Arrange the tendency for complex formation by alkaline earth metal ions (Be^{2+} , Mg^{2+} , Ca^{2+} , Sr^{2+} , Ba^{2+}) and explain it on the basis of their ionic potential. 3
- b) Compare and contrast the basic property and reducing property of group-15 (N, P, As, Sb, Bi) hydrides. 5
- c) What happens when ammonia gas is passed through CCl_4 or ether solution of S_2Cl_2 or SCl_2 at $\sim 50^\circ\text{C}$? 2
- d) Write down the products obtained from the reaction of B_2H_6 with NH_3 under different conditions of reactions. 3

UNIT - II

3. a) Draw the approximate energy level diagram for HF molecule. Discuss the polarity of HF molecule from the diagram. 3 + 1
- b) What do you understand by Intrinsic and Extrinsic semiconductors? Illustrate with examples. 3
- c) Give one example of each (name & formula) :
- σ -donor and π -acceptor ligand
 - π -donor and π -acceptor ligand
 - Bridging ligand
 - Uninegative bidentate ligand. 2
- d) Which of the following ligands will form the most stable complex with Cu^{2+} and why?
- NH_3 , $\text{H}_2\text{N} - \text{CH}_2 - \text{CH}_2 - \text{NH}_2$, $\text{H}_2\text{N} - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{NH}_2$ 2
- e) Write the I.U.P.A.C. nomenclature of $[(\text{NH}_3)_5\text{Cr}(\text{OH})\text{Cr}(\text{NH}_3)_5]\text{Cl}_5$ 1

4. a) Write notes on any *two* of the following : 2 × 3
- i) Metallic bonding
 - ii) Chelates and Innermetallic complex
 - iii) Flexidentate character of polydentate ligand.
- b) How many isomers are possible with the complex ion $[\text{Cr}(\text{en})_2\text{Cl}_2]^+$? Suggest a chemical pathway to elucidate the structures. 1 + 2
- c) What are the expected changes in bond order and bond distance that accompany the following ionization processes ?
- i) $\text{O}_2 \rightarrow \text{O}_2^+ + \text{e}^-$
 - ii) $\text{NO} \rightarrow \text{NO}^+ + \text{e}^-$ 3

CEMAT 23-IB

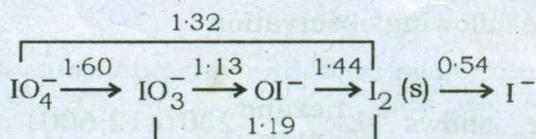
UNIT - I

5. a) What is inorganic benzene ? Discuss its structure and bonding. Give its preparation and uses. 1 + 2 + 2 + 1
- b) Give examples of the following with one chemical reaction of each : 2 × 1½
- i) Pseudohalide
 - ii) Interhalogen.
- c) What happens when CaF_2 is heated with conc. H_2SO_4 and SiO_2 in a dry test tube and fumes coming out were reacted with a water drop ? 1 + 3
6. a) What are NO_x ? Discuss the photochemical reactions of ozone in upper atmosphere. 1 + 3

- 2 × 3
- b) Give the general formula of the catenated oxyacids of sulphur. What will be the name of the species when $n = 3$? Mention the oxidation states of each sulphur present in the compound. 3
- c) Discuss the preparation, one reaction (oxidation or reduction or complex formation) and one important use of the following (any two) : 2 × 3
- i) Silicone
- ii) Hydroxylamine
- iii) Borax.

UNIT - II

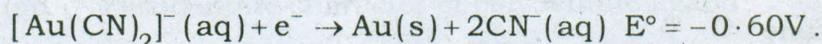
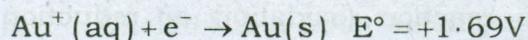
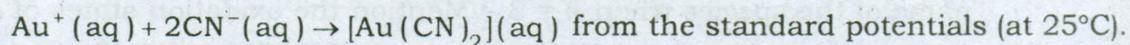
7. a) Define standard and formal potentials of a system. Which is more effective in the prediction of the course of a reaction? 3
- b) Calculate the solubility of CaF_2 in a solution of 0.1 M $\text{Ca}(\text{NO}_3)_2$.
[Given K_s of $\text{CaF}_2 = 4.9 \times 10^{-11}$]. 3
- c) What are the characteristics of redox indicators? Give one example of a redox indicator with its structure. 2 + 1
- d) $\text{Mn}^{2+}(\text{aq})$ is oxidised to MnO_4^- by sodium bismuthate in dil. HNO_3 medium. Balance the reaction by ion-electron method. 3
8. a) Calculate E° for the couple IO_3^-/I^- and hence its formal potential at $\text{pH} = 7$ from the following reduction potential diagram (Latimer diagram in acid medium, E° in volt) :



2 + 2

- b) Standard reduction potentials (E°) of $\text{Cu}^{2+}/\text{Cu}^+$ and $\frac{1}{2} \text{I}_2(\text{s})/\text{I}^-$ are + 0.15 volt and + 0.54 volt respectively. Indicate the oxidant and reductant in the two couple. Also indicate what actually happens during reaction with proper justification. [Given : $K_{sp}(\text{CuI}) = 1 \times 10^{-12}$] 2 + 2

- c) Calculate the equilibrium constant of the reaction



- d) 20 ml 0.1 (M) acetic acid is mixed with 10 ml 0.1 (M) NaOH solution. Find out the pH of the mixed solution. [Given : pKa (CH_3COOH) = 4.75]

Group - B

(Organic Chemistry)

CEMAT 23-OA

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

UNIT - I

1. a) Why is TMS chosen as reference compound in ^1H NMR spectroscopy ?

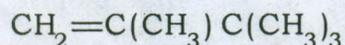
- b) A compound $\text{C}_4\text{H}_6\text{O}_2$ shows a very strong IR band at 1720 cm^{-1} and only one singlet signal in its ^1H NMR spectrum. Assign structure to the compound explaining the spectral data.

- c) Rationalize the following observation :

Mesityl oxide shows $\lambda_{\text{max}}^{\text{hexane}}$ 230 (ϵ 12,600) and 329 (ϵ 41) nm, but

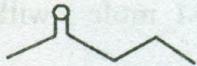
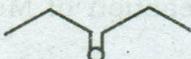
$\lambda_{\text{max}}^{\text{water}}$ 243 (ϵ 10,000) and 305 (ϵ 60) nm.

- d) Label the different types of magnetically non-equivalent hydrogens of the following compound and justify your answer :



e) How can you distinguish between the compounds in the following pairs by the methods as directed ?

i) Methyl benzoate and phenyl acetate by IR spectroscopy

ii)  and  by mass spectroscopy. 2 + 2

2. a) How is the O - H absorption peak in IR spectrum shifted by replacing H by D ? Give reasons. 2

b) The positions of UV absorption maxima of aniline in aqueous solution are different from those of benzene but the positions of UV absorption maxima of aniline in an acidic aqueous solution at pH = 1 are almost identical with those of benzene. Explain. 3

c) Toluene is oxidised to benzaldehyde. What change in the ^1H NMR spectral feature is observed in the product with respect to the starting compound ? 2

d) Distinguish between the compounds of the following pairs by the methods as directed :

i) *cis*-stilbene and *trans*-stilbene by UV spectroscopy

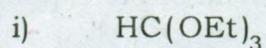
ii) CH_3CHBr_2 and $\text{CH}_2\text{BrCH}_2\text{Br}$ by ^1H NMR spectroscopy. 2 + 2

e) What are 'molecular ion peak' and 'base peak' in mass spectroscopy ? 2

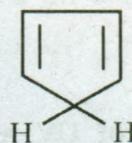
UNIT - II

3. a) Outline the stepwise conversion of benzene to phenol involving cumene as an intermediate product. Give the mechanism of the steps involved. 3

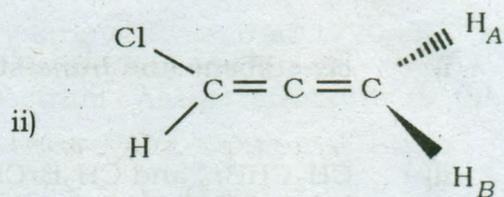
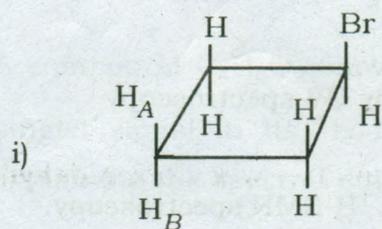
- b) Reimer-Tiemann reaction on *p*-cresol gives 2-hydroxy-4-methylbenzaldehyde along with a second product (A), which can also be worked up. Identify (A) and explain its formation.
- c) Give the product(s) of reaction of MeMgI (1 mole) with each of the following compounds :



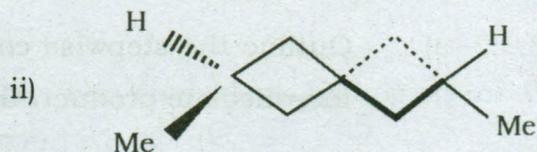
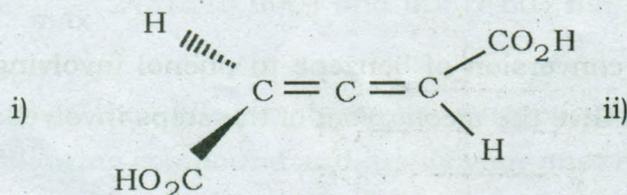
ii)



- d) Write the configuration of the product obtained by the substitution of pro-R hydrogen of propanoic acid by ethyl group.
- e) Identify H_A and H_B in each of the following molecules as homotopic, enantiotopic or diastereotopic with explanation :

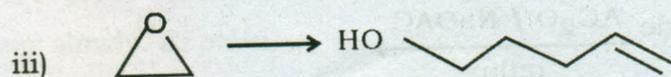
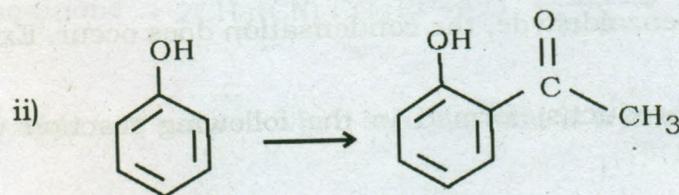
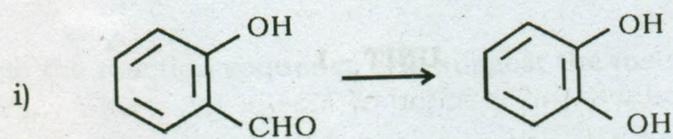


- f) Assign R/S descriptors to the following molecules :

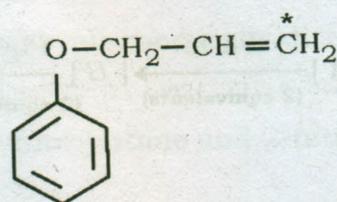


4. a) Carry out the following conversions and explain the reactions involved :

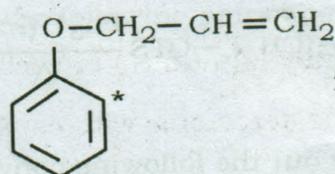
2 + 2 + 1½



- b) Write the structure of all possible products when a 1 : 1 mixture of



and

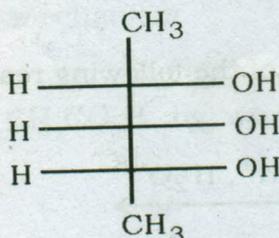


is heated together.

Explain their formation. ($C^* = {}^{14}C$)

- c) How would you resolve (\pm)2-octanol. 2
- d) Write the configuration of the product when acetaldehyde is reduced by the addition of H^\ominus to the re-face. 1
- e) Identify chirotopic/achirotopic carbon atoms in the following molecule :

1½

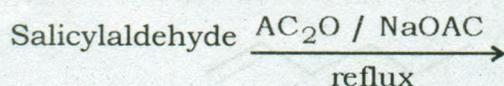


CEMAT 23-OB

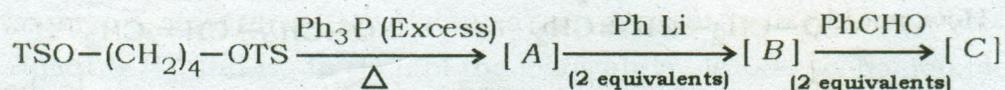
Attempt any *two* questions taking *one* question from each Unit.

UNIT - I

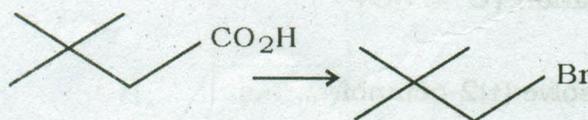
5. a) *p*-dimethylaminobenzaldehyde fails to undergo benzoin condensation but when mixed with benzaldehyde, the condensation does occur. Explain. 3
- b) Predict the product(s) formed in the following reaction with proper reaction mechanism : 3



- c) Write the structures of [A]; [B] and [C] : 3



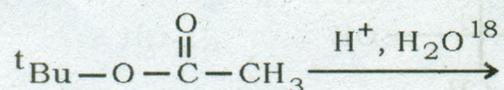
- d) Carry out the following conversion : 2



- e) Identify A and B and explain their formation : 2

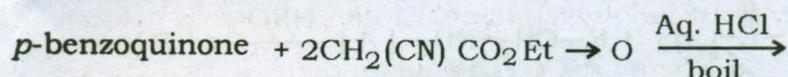


6. a) Predict the product(s) of the following reaction and give mechanism : 3



b) What happens when benzaldehyde is heated with acetic anhydride in the presence of sodium acetate? Write the mechanism of the reaction and explain the formation of styrene as one of the products. 3

c) Complete the reaction sequence and suggest the mechanism involved : 3



d) Explain what will happen when salicylic acid is treated with bromine water. 2

e) Acetyl chloride is readily decomposed by water, but benzoyl chloride reacts with water very slowly. Explain. 2

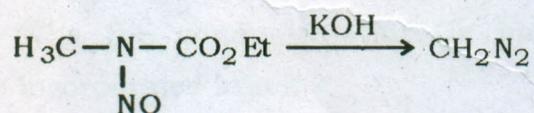
UNIT - II

7. a) How would you chemically distinguish the following pair of compounds : $2 \times 1\frac{1}{2}$

i) 1-nitrobutane and 2-nitrobutane

ii) Benzyl cyanide and benzyl isocyanide.

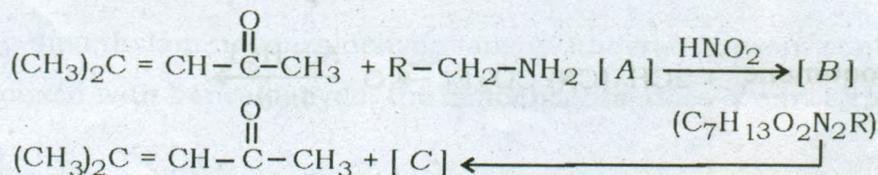
b) Give the mechanism of the following transformation : 2



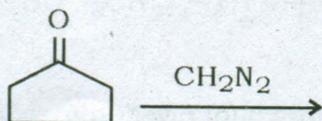
c) *p*-toluidine reacts with benzene diazonium chloride to form a compound which on boiling with dil. H_2SO_4 , gives four products (excluding nitrogen). Write the products with appropriate mechanism. 3

d) Convert $\text{CH}_3\text{CO}_2\text{H} \rightarrow \text{CH}_3\text{CH}_2\text{CO}_2\text{H}$ by using diazomethane and explain the conditions of the reaction. 2

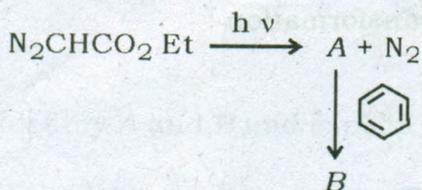
- e) Alkyl iodides on reaction with aqueous ethanolic KCN give mainly cyanides but isocyanides are the main products in their reactions with AgCN. Explain. 2
8. a) Complete the following equations assigning suitable structures from [A] to [C]: 3



- b) What would be the pH of the medium to get the best possible yield of the product if benzene diazonium chlorides allowed to undergo coupling reaction with N, N-dimethylaniline? Explain. 3
- c) Predict the product of the following reaction and suggest plausible mechanism: 3



- d) Write products A and B and explain the formation of B: 3



(OLD SYLLABUS)**Group - A****(Inorganic Chemistry)**

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

UNIT - I

1. a) With the help of Born-Haber cycle, calculate the electron affinity of hydrogen using the following data given in KJmol^{-1} :
- Sublimation energy of $\text{K(s)} = 83$, Ionization energy of $\text{K(g)} = 417$, bond dissociation energy of $\text{H}_2(\text{g}) = 436$, Lattice energy of KH(s) crystal = -742 , and heat of formation of $\text{KH(s)} = -59$. 4
- b) Using VSEPR theory predict the shapes of the following with reasons : 3 × 2
- i) BrF_4^-
- ii) XeF_6
- iii) XeOF_4
- c) HF is a monobasic acid, yet it forms KHF_2 . Explain. 2
- d) Why the conductivity of Ge increases many folds when trace of As is incorporated into it ? 2
- e) What is Bent's rule ? Explain. Predict the structure of PF_3Cl_2 with the help of Bent's rule. 1 + 1 + 2
2. a) Construct the approximate MO energy level diagram of carbon monoxide molecule. Calculate the bond order. Explain how it can act as a σ -donor ligand. 2 + 2 + 1
- b) Explain different lattice defects in ionic crystals with examples. 3

- c) Write the Born-Landé equation for an ionic crystal and also explain the terms used in it. Explain the limitations of the equation. 1 + 2 + 1
- d) What is an ambidentate ligand? How does it differ from a polydentate ligand? Give examples. 1 + 1 + 1
- e) Which one of the following will be more soluble in organic solvent and why? 1½
- i) TiCl_4
- ii) LiCl .
- f) AlF_6^{3-} is well known but BF_6^{3-} is not. Explain. 1½

UNIT - II

3. a) Give a comparative study of the chemistry of group 16 (VIB) elements with special reference to their — 3 × 3
- i) oxides
- ii) halides
- iii) oxoacids.
- b) Explain any *two* of the following : 2 × 2
- i) BeCl_2 forms polymer but AlCl_3 forms only up to dimer
- ii) MgCO_3 is thermally less stable than CaCO_3
- iii) Complex formation character of Group 2 (IIA) metal ions changes as $\text{Be}^{2+} > \text{Mg}^{2+} > \text{Ca}^{2+} > \text{Sr}^{2+} > \text{Ba}^{2+}$
- c) Comment on the stabilities of the different possible oxidation states of Cu, Ag and Au. 3
4. a) What happens when —
- i) CaF_2 is heated with conc. H_2SO_4 and SiO_2 in a dry test tube and the fumes coming out of the tube were placed in contact with a water drop?
- ii) An alkaline solution of sodium hypochlorite is added to a strong solution of ammonia containing a little gelatin? 2 × 2

- terms
2 + 1
and ?
1 + 1
? 1½

1½

with
- b) Compare the hydrolytic behaviour of NCl_3 and AsCl_3 , with reason. 2
- c) Comment on the feasibility of the following reaction with justification : 2

$$\text{PbCl}_4 \rightarrow \text{PbCl}_2 + \text{Cl}_2$$
- d) Trimethylamine is pyramidal but trisilylamine is planar. Explain. 2
- e) Give a comparative account of the chemistry of O, S, Se and Te with respect to the stability of their hydrides. 3
- f) Compare the chemistry of B and Al with reference to the diagonal relationship. 2
- g) Arrange the following ions in the increasing order of their oxidising power : 1
 ClO_4^- , BrO_4^- , IO_4^-

UNIT - III

5. a) Describe the preparation and one important use of the following : 2 + 2
 i) Red lead
 ii) Hydrazine.
- b) Describe the photochemical reactions of NO_x in the upper atmosphere and its impact on the environment. 3
- c) How is potassium bromate prepared ? 2
- d) What happens when borax is heated with methanol and concentrated H_2SO_4 ? 2
- e) Write short notes on the following : 2 + 2
 i) Sodium bismuthate
 ii) Carbides.
- f) Mention one laboratory use of tin-granules. 1
- x 3
x 2

Ag
3

he
?
on
2

6. a) Discuss the structure and bonding in any *three* of the following : 3 × 3
- i) Silicones or silicates
 - ii) Sulphur nitrogen compounds
 - iii) Xenon fluorides
 - iv) B_2H_6 .
- b) Perchloric acid is stronger acid than HOCl. Explain. 2
- c) How is ultrapure Germanium prepared ? Mention one use of it. 2 + 1
- d) Iodine is more soluble in H_2O in presence of I^- ions. Explain. 2

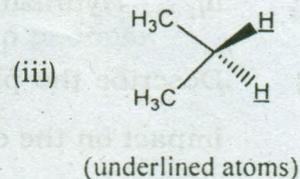
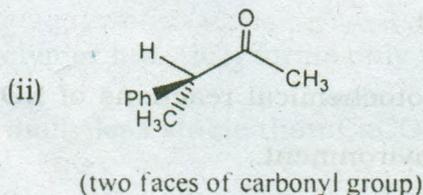
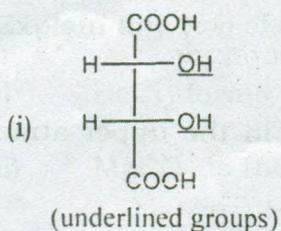
Group - B

(Organic Chemistry)

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

UNIT - I

1. a) Indicate the topic relationship between the atoms or groups or faces as indicated in the parenthesis in the following molecules : 3



- b) Draw the energy profile diagram for the rotation across C-C bond of biphenyl system of 6, 6'-dinitrodiphenic acid. 2
- c) Outline the procedure for the resolution of (\pm) 2-octanol. 2
- d) How can you distinguish the following compounds by the spectroscopy as indicated in the parenthesis ? 3 × 2
- i) Phenyl acetate and methyl benzoate (IR spectroscopy)
 - ii) *Cis* and *trans* stilbenes (UV spectroscopy)
 - iii) Phenol and anisole (UV spectroscopy).
- e) Write down Pschorr synthesis of phenanthrene. 3

3 x 3

2. a) Explain any *two* of the following terms : 2 x 1½

i) Chemical shift

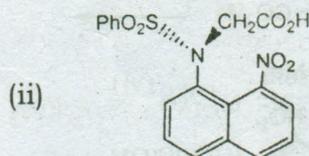
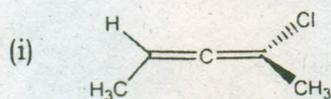
ii) Deshielding effect

iii) Fingerprint region.

b) Which criteria help TMS to act as an internal standard ? 2

c) Draw a neat sketch of ^1H NMR spectrum of CH_3CHBr_2 indicating shielding/deshielding protons, integration and spin-spin coupling. 3

d) Assign R/S configuration of the following compounds : 2



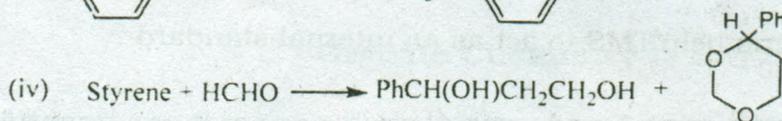
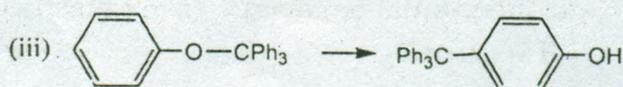
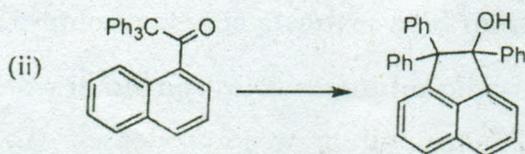
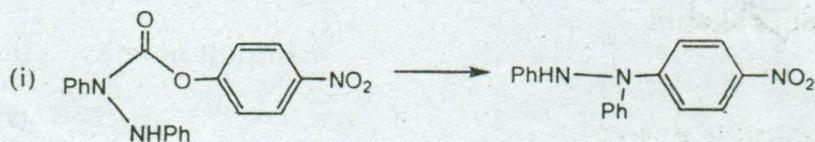
e) What is optical purity ? The specific rotation of a pure optically active compound is 80° . Calculate the % of (+) and (-) isomers of this compound in a mixture, which shows a specific rotation of 20° . 3

f) Phenanthrene is more alkene-like and anthracene is more diene-like. Explain with examples. 1½ x 2

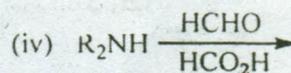
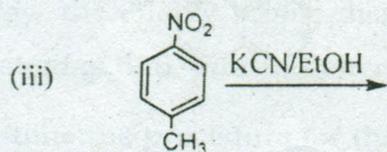
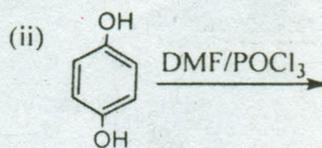
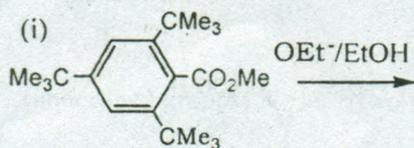
3

UNIT - II

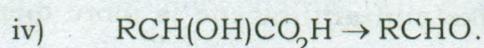
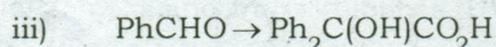
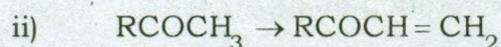
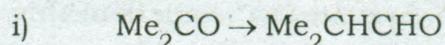
3. a) Suggest the reagents used in the following transformations and write the mechanism (any three) : 3 × 2



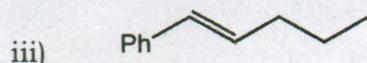
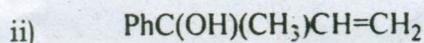
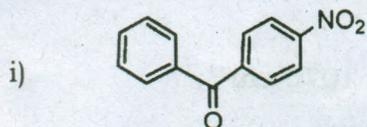
- b) Explain the differential behaviour of PhONa and PhOK towards CO₂ under high pressure. 3
- c) CH₃CO₂Et but not Me₂CHCO₂Et undergoes Claisen condensation on treatment with NaOEt. Explain the fact showing the mechanism of Claisen condensation. 3
- d) Predict the products of the following reactions giving mechanism (any three) :



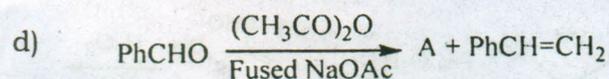
4. a) Carry out any three of the following transformations : 3 × 2



- b) Give the retrosynthetic pathways and one efficient synthetic methods for the following compounds (any two) : 2 × 3



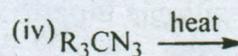
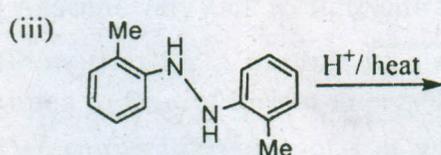
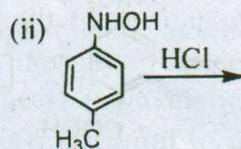
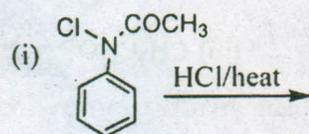
- c) Discuss the bromination of 2-butanone (i) in presence of acid and (ii) in presence of base. Explain the differential behaviour giving mechanism. 3



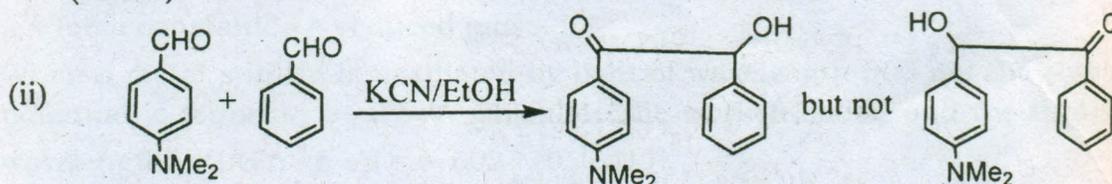
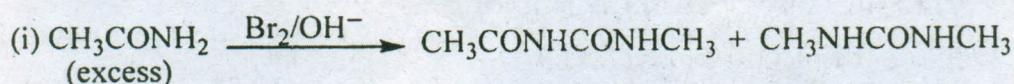
Write the structure of A and write down the mechanism for the formation of A and PhCH=CH_2 . 3

UNIT - III

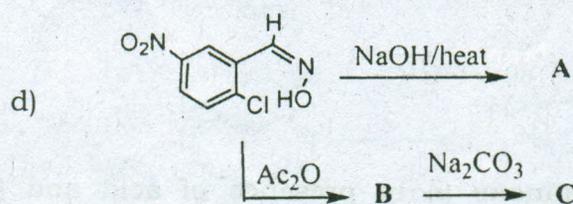
5. a) Predict the major products only and write mechanism to show their formation (any three) : 3 × 2



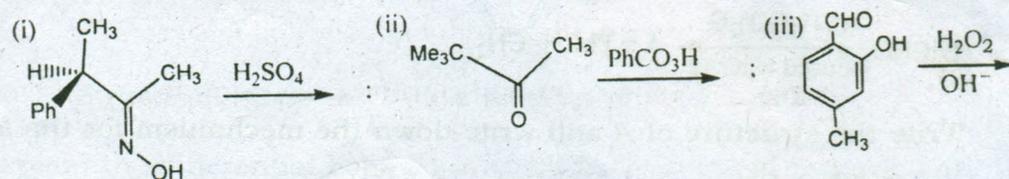
- b) Write down the mechanism of the following reaction : 2 × 2



- c) A compound having molecular formula $C_8H_{18}O$ exhibits the following spectral data. Identify the structure of the compound : 3
 UV : Transparent above 210 nm
 IR : Bands at 2960-2851 (m), 1342 (w) and 1075 cm^{-1} ;
 $^1\text{H NMR}$: Only one singlet at $\delta 1.05$.



6. a) Complete the following reactions with mechanism (any four) : 4 × 3



- b) Carry out the following transformations (any two) (mechanism not required) : 2 × 2

