

## West Bengal State University

B.A./B.Sc./B.Com. ( Honours, Major, General ) Examinations, 2012

## PART-II

## CHEMISTRY — Honours

## Paper-III

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 script for each Group.

## GROUP - A

## ( INORGANIC CHEMISTRY )

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

## UNIT - I

1. a) Indicate the state of hybridisation of the central atom and shape of the following molecules : ( any two ) 2 × 2 = 4
- i)  $\text{POCl}_3$
- ii)  $\text{IF}_5$
- iii)  $\text{ICl}_2^-$ .
- b) Draw the approximate MO energy level diagram for NO molecule. Compare the bond dissociation energies of  $\text{NO}^+$  and  $\text{NO}^-$  and explain the difference. 2 + 2
- c) Explain, with example, dipole-dipole interaction and ion-dipole interaction. 2 × 1½ = 3
- d) What is the expected structure of solid AgCl from the radius ratio values ? 2
- e) When Ge is doped with Ga it becomes a *p*-type semiconductor. Explain. 2



- f) Calculate the electron affinity of chlorine from the following data : ( energies in  $\text{kJmol}^{-1}$  )

Heat of formation of  $\text{MCl}_{(s)} = -441$ ; Heat of sublimation of  $\text{M}_{(s)} = 80$ ; Bond dissociation energy of  $\text{Cl}_2 = 242$ ; I.P of  $\text{M}_{(g)} = 403$  and the lattice energy of  $\text{MCl}_{(s)} = -680$ . 3

2. a) Explain any *two* : 2 × 2 = 4
- i) Magnesium oxide has a higher melting point than sodium fluoride.
  - ii)  $\text{HgI}_2$  is much less soluble in water than  $\text{HgCl}_2$ .
  - iii) Melting point of  $\text{AgCl}$  is  $455^\circ\text{C}$  while that of  $\text{KCl}$  is  $776^\circ\text{C}$  though the radii of  $\text{K}^+$  and  $\text{Ag}^+$  ions are comparable.
- b) Define different types of lattice defects with example. 4
- c) Using VSEPR theory predict the shapes of the following with reasons : 2 × 2 = 4
- i)  $[\text{AsH}_4]^+$
  - ii)  $\text{PCl}_5$ .
- d) State the name and formula of an optically active octahedral complex and a square planar complex. 2
- e) The dipole moment of carbon monoxide molecule is much smaller than expected and the negative end of the dipole lies on the less electronegative carbon. Explain. 4

### UNIT - II

3. a) Give a comparative account of the chemistry of group ( 15 ) elements with special reference to their
- i) Oxidation states ( with example )
  - ii) Oxides and
  - iii) Hydrolytic behaviour of their halides. 3 × 3 = 9
- b) Explain any *two* of the following : 2 × 2 = 4
- i) Water shows anomalous expansion in the temperature range  $0^\circ\text{C} - 4^\circ\text{C}$ .
  - ii) Iodine is more soluble in water in presence of an iodide salt.
  - iii)  $\text{NH}_3$  is more reducing than  $\text{PH}_3$ .
- c)  $\text{SiCl}_4$  hydrolyses readily but  $\text{CCl}_4$  does not. Explain with reasons. 3



4. a) Write an account of the diagonal relationship of lithium and magnesium. 3
- b) Indicate the feasibility of most common and also the highest oxidation states possible for Cr, Mn and Fe. 3
- c) A chlorine derivative corresponding to  $\text{KHF}_2$  is not known. Explain. 2
- d) What is inert pair effect? How does this effect influence the chemical properties of Sn and Pb of group 14? 3
- e) What happens when ammonium molybdate solution is added to an excess of concentrated nitric acid solution of  $\text{NaH}_2\text{PO}_4$ ? Give balanced equation. 2
- f) Give an account of oxides and oxyacids of group 17 elements in periodic table. 3

**UNIT - III**

5. a) Discuss the structure and bonding in  $\text{B}_2\text{H}_6$  molecule in the light of MO and VB theories. 5
- b) How is ultra pure silicon prepared? Mention one of its uses. 3
- c) Describe the principle of extraction of Lithium from its ore. Give one of its uses. 4
- d) Give the preparation and any one important use of the following ( any two ) :  $2 \times 2 = 4$
- i) Stanous chloride
- ii) Perchloric acid
- iii) Lead tetracetate.
6. a) How argon can be isolated from air? 2
- b) Give a short note on hydrazoic acid. 2
- c) What are the products of reaction of diborane with ammonia, at different temperatures? 4
- d) State the main structural difference between dithionic acid and polythionic acid. 2
- e) "Cyanogen is a pseudo halogen." Justify. Give chemical equations. 4
- f) State why  $\text{SO}_2$  is a discrete molecule but  $\text{SeO}_2$  is polymeric. 2

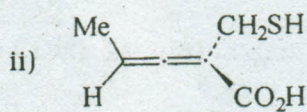
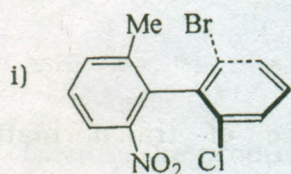


## GROUP - B

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

## UNIT - I

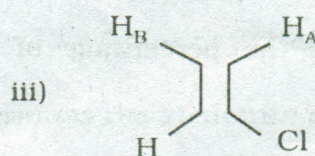
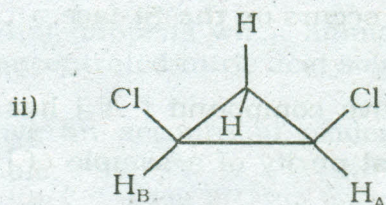
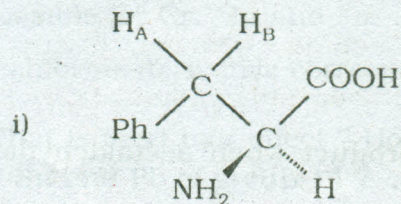
1. a) Draw the absolute configuration of the product when acetaldehyde is treated with  $\text{PhMgBr}$  assuming nucleophilic attack occurs on the Si-face. 2
- b) Pure ( - ) enantiomer of an optically active compound [ A ] has a specific rotation  $[\alpha]_{\lambda}^{20} = -51.3$ . What is the optical purity of a sample of [ A ] which shows specific rotation of  $-35.9$  ? Calculate the percentage of the major enantiomer in the sample [ A ]. 2
- c) Assign R/S configurational descriptors to the following molecules : 2



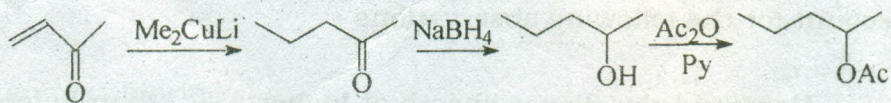
- d) Account for the following observations : 2 + 2 = 4
- i) Homoannular dienes absorb at higher  $\lambda_{\text{max}}$  than heteroannular dienes.
- ii) The  $-\text{OH}$  stretching of phenol appears at higher wave number in carbon tetrachloride solution than in benzene solution.
- e) Compound A ( molecular formula  $\text{C}_6\text{H}_{12}\text{O}$  ) shows a peak at  $1715\text{ cm}^{-1}$  in its IR spectrum. The PMR spectrum of compound A displays two singlets at  $\delta$  0.9 and 2.2 in the ratio of 3 : 1. Deduce a structure for compound A that fits these spectroscopic data. 3
- f) How can you convert toluene into 1, 7-dimethylnaphthalene ? 3



2. a) Indicate the topic relationship between  $H_A$  &  $H_B$  in each of the following structures :



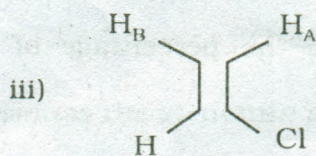
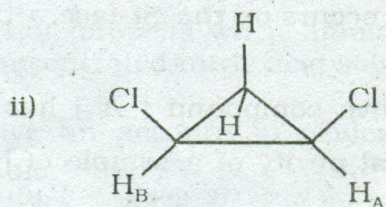
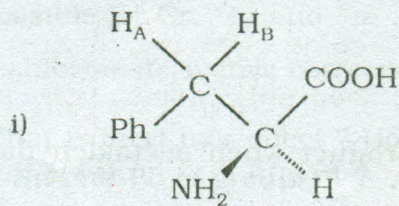
- b) *R*-2-phenyl propanoyl chloride loses its optical activity on treatment with triethyl amine. Explain.
- c) How can you trace the following sequence of transformations using IR spectroscopy ?



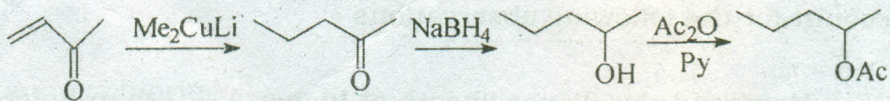
- d) Acetylenic protons appear at lower  $\delta$  value than ethylenic protons despite the higher electronegativity of acetylenic carbons than ethylenic carbons. Explain.
- e) How would you distinguish between *cis*- and *trans*-1, 3, 5-hexatriene using UV-spectrum.
- f) Write down the structure of the compound  $C_5H_{11}Cl$  which shows two signals in its  $^1H$ -NMR spectrum. Predict the chemical shifts.
- g) How naphthalene can be converted to anthracene ?



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## UNIT - II

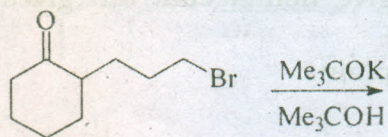
3. a) Explain the following observations : 3 × 3 = 9

i) *p*-nitrobenzaldehyde fails to undergo benzoin condensation but *o*-nitrobenzaldehyde can respond to benzoin condensation.

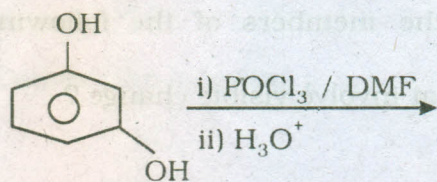
ii) Reaction between potassium phenoxide and allyl bromide in dry acetone gives allyl phenyl ether as the major product but use of benzene instead of acetone as solvent in the same reaction furnishes 2-allyl phenol as the major product.

iii) Alkaline hydrolysis of *S*-1-phenyl ethyl acetate gives *S*-1-phenyl ethanol but acid hydrolysis of the same ester affords racemic 1-phenyl ethanol.

b) Identify the three products in the following reaction and suggest mechanism for their formation. ( All the products contain two ring systems ) 4

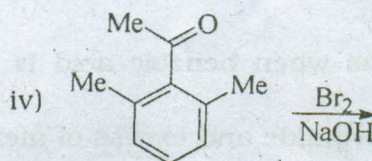
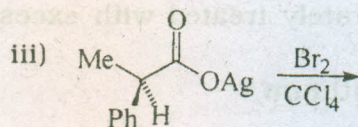
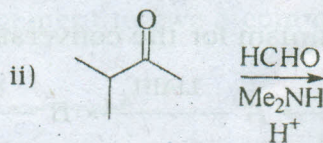
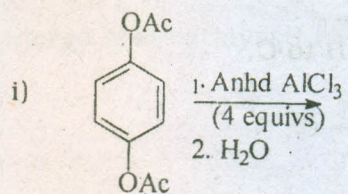


c) Identify the product with plausible mechanism : 3



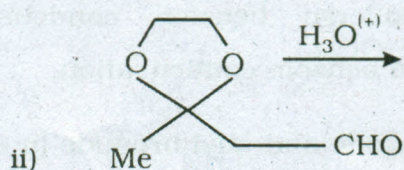
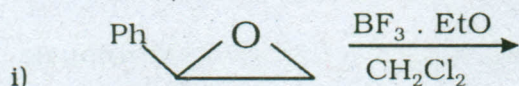
d) Convert  $\text{PhCHO} \rightarrow \text{PhCDO}$ . 2

4. a) Predict the products in each of the following reactions and suggest mechanism in each case ( any three ) : 3 × 3 = 9

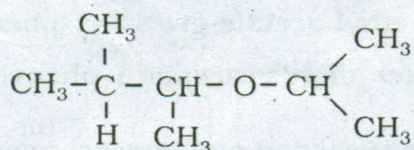




- b) Predict the products with plausible mechanism in the following : 2 + 2 = 4



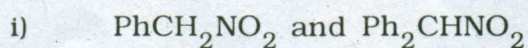
- c) Can you prepare the following compound by Williamson synthesis ? Explain your answer and suggest a feasible method for its effective synthesis. 3



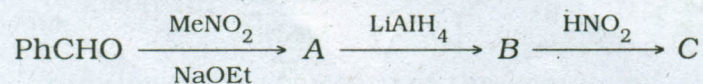
- d) Chloral reacts rapidly with ethanol to give hemiacetal, but gives acetal very slowly in presence of anhydrous acid. Explain. 2

### UNIT - III

5. a) How can you distinguish between the members of the following pairs of compounds with chemical reactions that involve visible change ? 2 + 2 = 4



- b) Identify the products A - C in the following sequence of transformations. Suggest a mechanism for the conversion of B to C. 4



- c) What happens when benzoic acid is separately treated with excess of methyl magnesium bromide and excess of methyl lithium ? 2



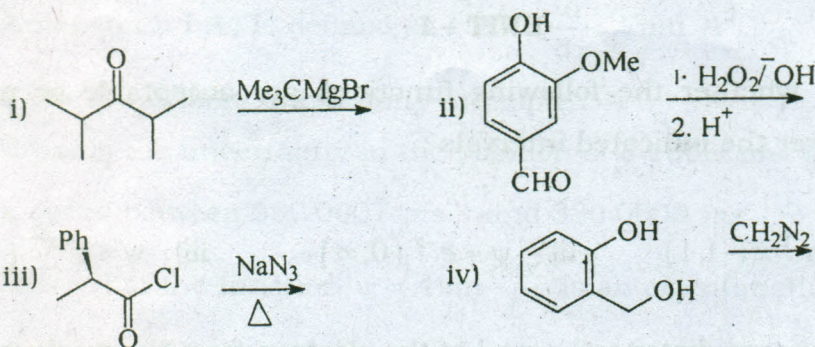
d) Account for the following observations : 2 × 2 = 4

i) Benzene diazonium chloride fails to couple with anisole but 2, 4-dinitro benzene diazonium chloride can couple with anisole.

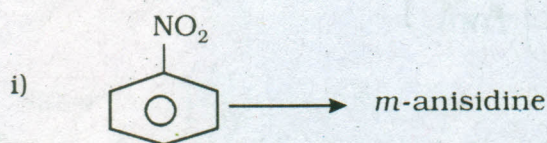
ii) Reaction of allyl bromide with magnesium in dry, alcohol free ether gives allyl magnesium bromide but the same reaction using lithium instead of magnesium leads to the formation of 1, 5-hexadiene.

e) "In the Arndt-Eister synthesis two equivalent of diazomethane is used." Explain the statement showing mechanism of the reaction. 2

6. a) Predict the product(s) in the following reactions and suggest plausible mechanism in each case ( any three ) : 3 × 3 = 9



b) Convert the following : 2 × 2  $\frac{1}{2}$  = 5



ii) *o*-xylene → Anthranilic acid.

c) The isomeric pinacols  $\text{Ph}_2\text{C}(\text{OH})\text{C}(\text{OH})\text{Me}$  and  $\text{PhMeC}(\text{OH})\text{C}(\text{OH})\text{PhMe}$  undergo acid catalysed rearrangement to give a common product. Explain. 2