



CHE (H) - II
P-III

CEMA(HN)-03

West Bengal State University

B.A./B.Sc./B.Com. (Honours, Major, General) Examinations, 2015

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 scripts for [CEMAT-23-IA & CEMAT-23-IB

and CEMAT-23-OA & CEMAT-23-OB]

Group - A

CEMAT-23-IA

Answer any four questions, taking one from each Unit.

UNIT - I

1. a) Discuss and compare the characteristics of H_2M ($M = S \text{ \& \; Se}$) in terms of (i) acidic behaviour and (ii) reducing character. 2 × 2 $\frac{1}{2}$
- b) The formula of telluric acid (H_6TeO_6) is different from selenic acid (H_2SeO_4). Justify. 2
- c) Why is NF_3 inert to hydrolysis but NCl_3 is not? 2
- d) $SnCl_2$ is a solid while $SnCl_4$ is a liquid, why? 2
- e) Why does Lithium behave as the most powerful reducing agent in aqueous solution? 2

SUB.-B.Sc.(HN)-CEMA-6008

[Turn over

2. a) Give a comparative study of oxy-acids of sulphur in terms of (i) Hybridization state of central element and (ii) Acidic strength. 3×2
- b) Compare the stability of PbCl_2 and PbCl_4 w.r. to inert pair effect. Draw the structure of anhydrous SnCl_2 in gas phase as well as in crystalline phase. $2 + 2$
- c) Elucidate noticeable properties that are developed when alkali metals or alkaline earth metals are dropped in liquid NH_3 . 3

Unit - II

3. a) Draw M.O. diagram of CN^- and predict the bond order as well as magnetic properties. 3
- b) Write down IUPAC — system name of
- $$\left[(\text{NH}_3)_3 \text{Co} \begin{array}{c} \diagup \text{OH} \diagdown \\ \text{— OH —} \\ \diagdown \text{OH} \diagup \end{array} \text{Co}(\text{NH}_3)_3 \right]^{3+}$$
- 2
- c) Why are glass apparatus dried by cleaning with alcohol or acetone? Which one is more effective and why? 2
- d) Among the various geometrical isomers of $[\text{Co}(\text{en})_2\text{Cl}_2]$, predict the optical isomers. 2
- e) Distinguish between $[\text{Pt}(\text{NH}_3)_4\text{Cl}_2]\text{Br}_2$ and $[\text{Pt}(\text{NH}_3)_4\text{Br}_2]\text{Cl}_2$ by chemical test. What type of isomerism exists between them? $2 + 1$
4. a) What is the basic difference between semiconductors and superconductors? Mention two types of extrinsic semiconductors with examples. $2 + 1$
- b) What is ambidentate ligand? Give examples of two complexes where such ligands are used. $2 + 1$

- c) Predict which one between $K_3 [FeF_6]$ and $K_3 [Fe(CN)_6]$ is paramagnetic & inner metallic complex. 2
- d) Give the MO description of NO molecule. Though it contains one unpaired electron but it is stable. Moreover the bond in NO^+ is short and strong. Explain. 3

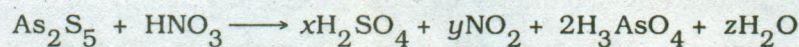
CEMAT-23-IB

Unit - I

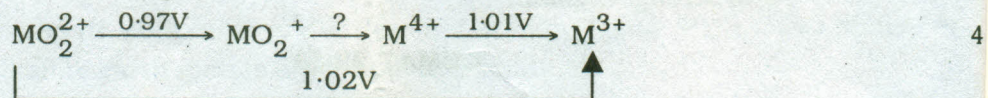
5. a) How many types of interhalogen compounds are formed by iodine and fluorine ? Why are interhalogens more reactive than pure halogen molecules ? 1 + 2 + 1
- b) Quantitative estimation of N_2H_4 is done using standard $KBrO_3$ in acid medium. Write the proper chemical reaction for such estimation and also indicate the colour at equivalence point. 3 + 1
- c) What are silicones ? Write the proper structure of silicone produced when CH_3SiCl_3 is carefully hydrolysed under controlled heating. 1 + 3
- d) Why $XeOF_4$ cannot be stored in glass or quartz container ? 1
6. a) Mention a convenient and less hazardous route to synthesize $XeOF_4$. Mention its reactions. 3
- b) What products are obtained when ICl is hydrolyzed under proper chemical conditions ? 2
- c) Sodium thiosulphate solution is used as fixer for developing work in photography. Write the chemical reactions involved in the process. 2
- d) Why is $B_3N_3H_6$ called inorganic benzene ? Mention the hybridization state of B and N in the compound. 2 + 2
- e) H_2O_2 behaves both as oxidant as well as reductant. Give one example for each case and establish involving half reactions. 2

Unit - II

7. a) Find the value of coefficients of the following redox reaction : 2



- b) Calculate E° for $\text{MO}_2^+ \longrightarrow \text{M}^{4+}$ in 1M acid medium from the following Latimer diagram :



- c) Discuss the solubility product principle. Explain how the principle is utilised in the precipitation of Gr IIIB (Co^{2+} , Ni^{2+} , Mn^{2+} and Zn^{2+}) cations. 4
- d) For the reaction $2\text{Cu}^+ \rightleftharpoons \text{Cu}^0 + \text{Cu}^{2+}$ in aqueous medium the value of $K_c = 1 \times 10^6$. Addition of slight excess of CN^- ion results $K_c \sim 1 \times 10^{30}$. Justify the result. 2

8. a) Calculate the emf of the cell :
Pt, H_2 (1 atm) | 0.1 N HCl || 1N KOH | H_2 (1 atm), Pt, provided 0.1 N HCl is 90% ionized and 1N KOH is 75% ionized. Also comment on the result. 3
- b) How does BDS act as redox indicator during titration of Fe^{2+} solution by standard $\text{K}_2\text{Cr}_2\text{O}_7$ solution in concentrated H_2SO_4 medium ? 2
- c) Give the disproportionation of chlorous acids and its salts in ion-electron balance method. 2
- d) A silver electrode is immersed in saturated Ag_2SO_4 solution. The potential difference between the Ag and normal H-electrode is found to be 0.711 volt at 25°C . Determine K_{sp} of Ag_2SO_4 . 4

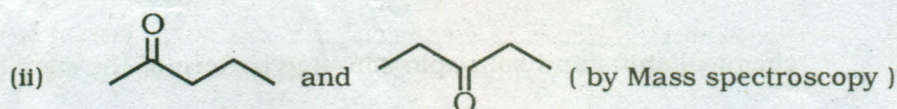
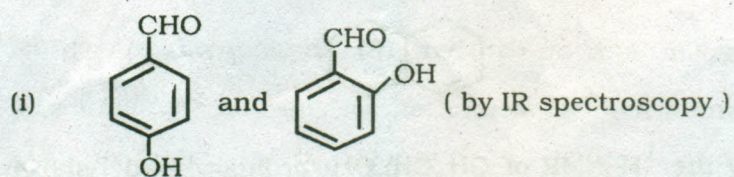
Group - B

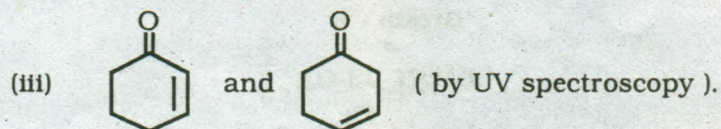
CEMAT-23-OA

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

Unit - I

9. a) The UV spectrum of mesityl oxide shows absorption bands at 230 nm ($\epsilon=12600$) and 329 nm ($\epsilon=41$) in hexane. Assign them in terms of electronic transitions. How do the absorption bands change their positions in water as solvent? 3
- b) What do you mean by the following terms? (any *two*) 2 + 2
- (i) Molecular ion/peak
- (ii) Fingerprint region
- (iii) Magnetically non-equivalent protons.
- c) Why is TMS used as reference compound in scanning $^1\text{H-NMR}$ spectrum of a compound? 2
- d) Compare the $\text{C}=\text{O}$ stretching frequencies of acetone and hexamethyl acetone and explain. 2
- e) How would you distinguish between *o*-xylene and *p*-xylene by $^1\text{H-NMR}$ spectroscopy? 2
10. a) How would you distinguish between the members in each of the following pairs of compounds using the spectroscopic techniques mentioned within parenthesis? (any *two*) 2 x 2





- b) Compound A (C_3H_8O) shows the following spectral pattern :

UV : transparent above 200 nm :

IR (cm^{-1}) : 3410, 2950, 1275, 1045.

1H -NMR : δ 4.58 (1H, broad singlet), 3.6 (2H, triplet),

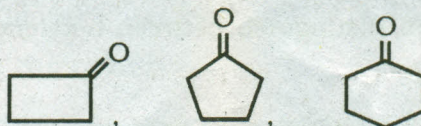
1.90 (2H, sextet), 1.0 (3H, triplet).

Deduce the structure of the compound A.

3

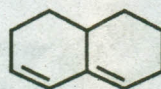
- c) Arrange the following compounds in their increasing order of 'C = O' stretching frequency and rationalize ;

2



- d) Calculate the λ_{max} of the following compound in UV spectroscopy.

2

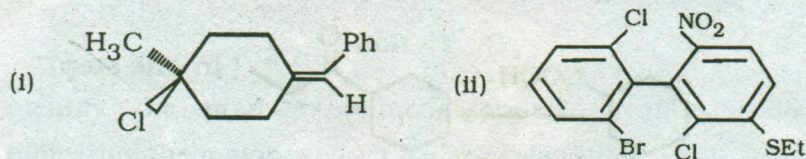


- e) Draw the 1H -NMR of CH_3CH_2OH (ordinary grade) showing the relative chemical shifts and spin-spin coupling pattern of the signals.

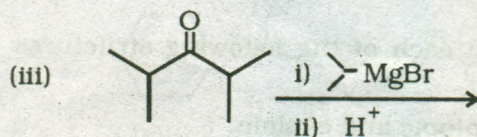
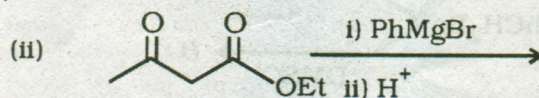
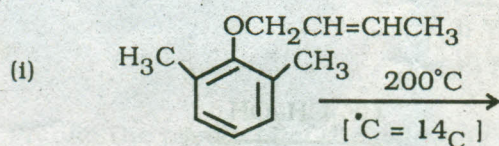
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UNIT-II

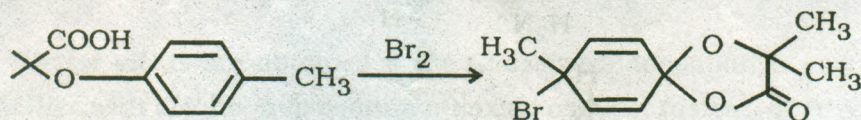
11. a) Find out (R/S) configuration for the following compounds. 2



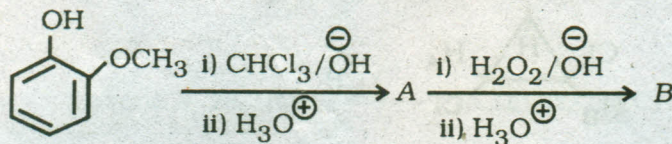
- b) Predict the product(s) in the following reactions and suggest mechanisms for their formation. 3 x 2



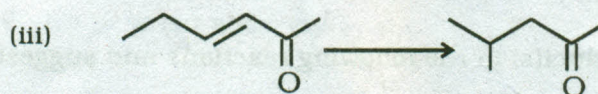
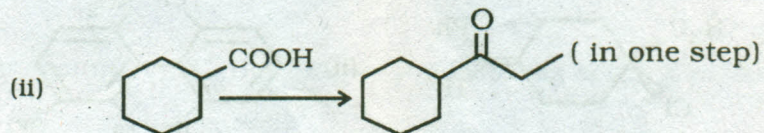
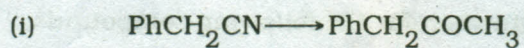
- c) How can you resolve (\pm) 2-aminopropanoic acid? 2
- d) Suggest a mechanism for the following reaction. 2



12. a) Identify the compounds (A) and (B) in the following sequence of transformations and suggest mechanism for their formation. 4

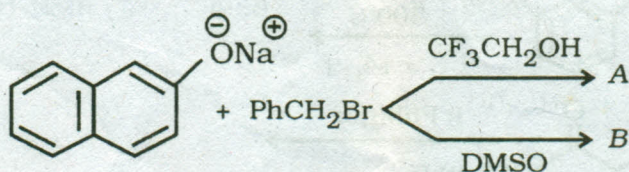


b) How can you carry out the following transformations ?



c) Predict the products :

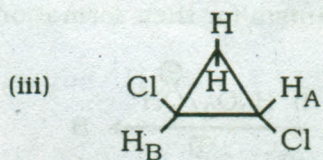
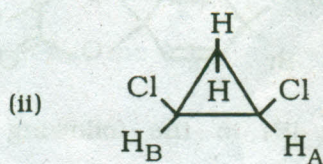
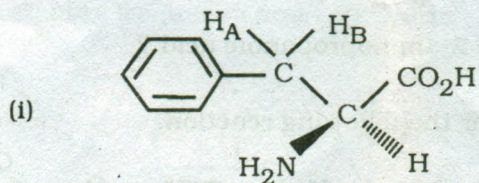
1 +



d) Identify H_A and H_B in each of the following structures as homotopic

enantiotopic or diastereotopic and explain.

1 + 1 +

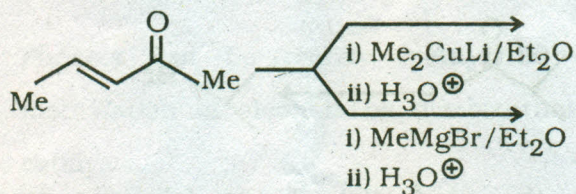


CEMAT-23-OB

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

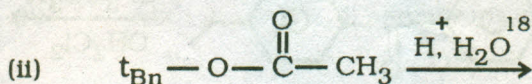
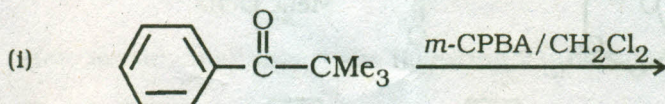
Unit - I

13. a) Identify the product/products formed in the following reactions, indicating the major product. Offer explanation. 3

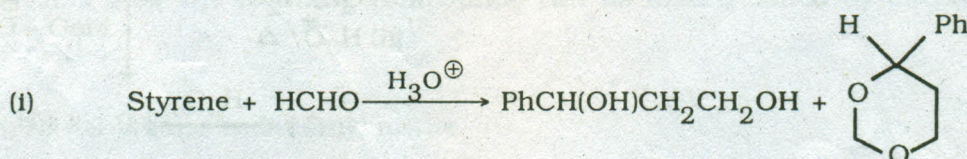


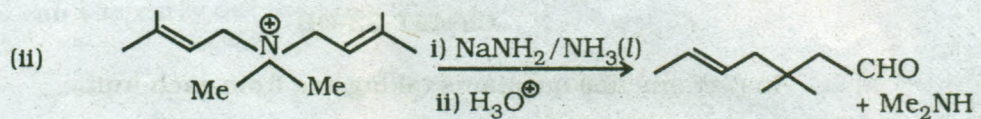
- b) Predict the products of the following reactions and give mechanisms :

$$2 \times 1 \frac{1}{2} = 3$$

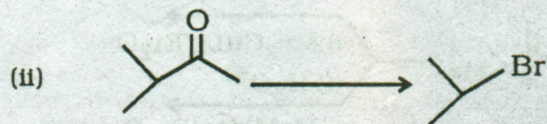
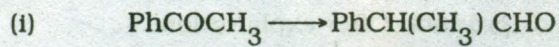


- c) Which of the following compounds will reduce Fehling's solution faster ? *p*-dimethylaminobenzaldehyde or $\text{Me}_2\text{N}(\text{CH}_2)_6\text{CHO}$. Explain. 2
- d) "Better yields are obtained if the Claisen condensation is carried out in ether with alcohol free sodium ethoxide catalyst instead of ethyl alcohol." Explain. 2
- e) Give mechanism of the following reactions : 2 × 1 $\frac{1}{2}$

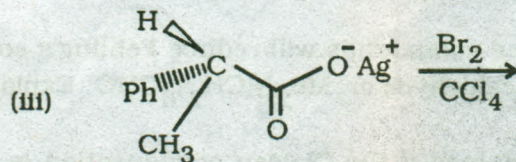
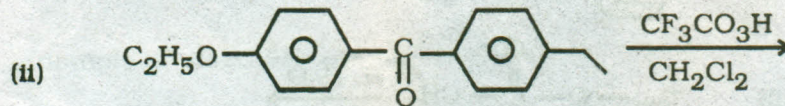
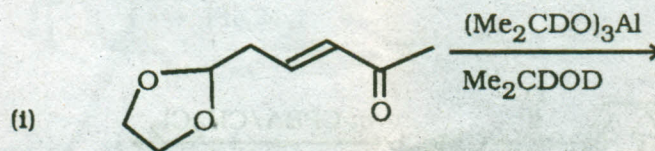




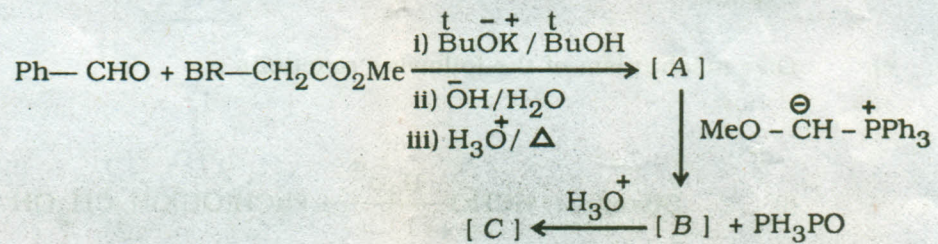
14. a) How can you achieve the following transformation? (any one) $2 \frac{1}{2}$



b) Indicate the product(s) of the following reactions with plausible mechanisms. $3 \times 2 = 6$



c) Predict the products and explain their formation with mechanism. $1 \frac{1}{2} + 3$



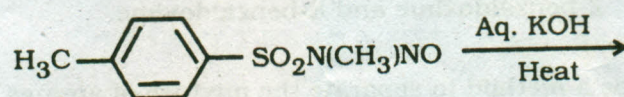
Unit - II

15. a) Explain the following observations : 2 + 2

(i) Benzene diazonium chloride couples with phenol in alkaline medium but not with anisole (PhOCH_3) under the same reaction conditions.

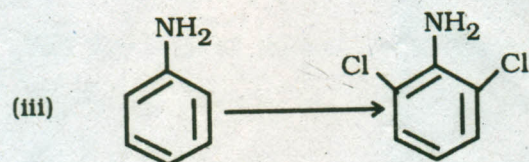
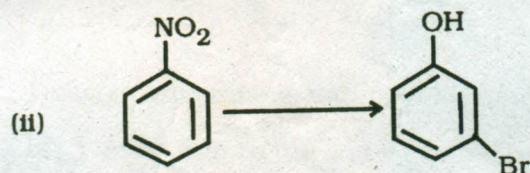
(ii) Phenols can be readily methylated by diazomethane but methylation of alcohols by diazomethane requires Lewis acid catalysis.

b) Give the product and mechanism of the following reaction : 2



c) How would you convert the following ? (any two) 2 + 2

(i) Aniline \rightarrow 1, 2, 3 - tribromobenzene.

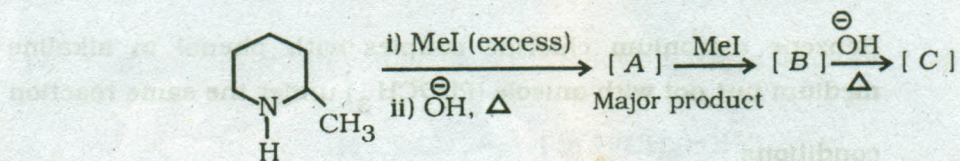


d) Show how the following compounds can be distinguished by chemical method. 2

Nitromethane and methyl nitrite.

16. a) Describe a convenient method for synthesizing diazoacetic ester. 2

b) Explain the following reaction sequence identifying [A], [B] and [C]. 3



c) Distinguish between the members of the following pairs by suitable chemical reactions. 2 + 2

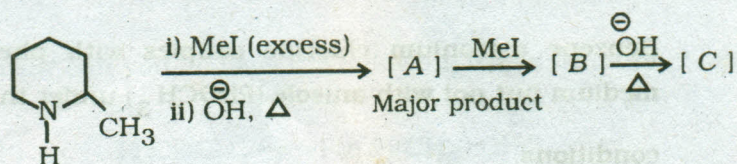
(i) PhCH_2NO_2 and *p*-nitrotoluene

(ii) *Z*-benzaldoxime and *E*-benzaldoxime.

d) Describe a method to separate the mixture of amines (1°, 2° and 3°). 3

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