

2019

CHEMISTRY

PAPER-II

Time Allowed — 3 Hours

Full Marks — 200

If the questions attempted are in excess of the prescribed number, only the questions attempted first up to the prescribed number shall be valued and the remaining ones ignored.

Answer may be written either in English or in Bengali but all answers must be in one and the same language.

Section-I

This section comprises 15 questions in three Groups. Answer any ten questions taking at least three questions from each Group.

Group – A

4×5

1. Explain the reaction of $Mn_2(CO)_{10}$ with molecular Hydrogen. Discuss the type of reaction involved.
2. Carry out the reaction of ferrocene with dilute nitric acid. How would you perform the nitration of ferrocene?
3. Cyanide occupies very high position in the Nephelauxetic series of ligands.—Explain.
4. Discuss the role of [4Fe, 4S] Ferredoxins in electron transport.
5. Draw the possible geometrical isomers of $\left[Pt^{IV} Cl_2 (NH_3)_2 Br_2 \right]$ and hence explain which of them will be optically active.

Group – B

4×5

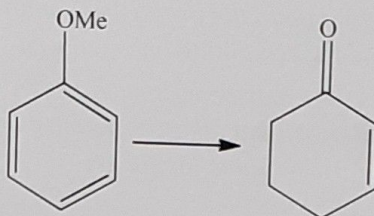
6. Draw a labelled phase diagram of a two component solid-liquid equilibrium system and hence explain what is meant by an eutectic mixture.
7. Briefly explain the difference between Fluorescence and Phosphorescence.
8. What is a zero order reaction? Explain with an example.
9. Why the word 'average' is used in the molecular weight of a polymer?
10. Write down the basic assumptions of collision theory.

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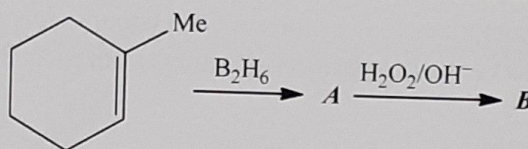
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Group - C

11. *Trans*-cyclo octene is chiral. Explain its nature of chirality. 4x5
12. Draw the enantiomers of *trans*-2-methylcyclohexanol. Assign R/S configuration to the asymmetric centres.
13. How can you carry out the following conversion?



14. Identify the products **A** and **B** of the following reactions. Indicate their stereochemistry.



15. Treatment of active *threo* isomer of 3-bromo-2-butanol with HBr gives *dl*-2,3-dibromobutane exclusively. Explain.

Section-II

This section comprises six questions in three Groups. Answer any four questions taking at least one questions from each Group.

Group - A

16. (a) Explain why $[CoCl_4]^{2-}$ and $[Co(H_2O)_6]^{2+}$ complexes have magnetic moment higher than the spin only value. 8
- (b) Give the IUPAC names of 2x4=8
- (i) $[Co(bpy)_3]_2(SO_4)_3$
 - (ii) $[Fe(\eta^5-C_5H_5)_2]$
 - (iii) $[Ir(Co)Cl(PPh_3)_2]$
 - (iv) $[(Co)_3Fe(Co)_3Fe(Co)_3]$
- (c) Discuss the structure and bonding in $k[PtCl_3(\eta^2-C_2H_4)]$ with suitable experimental evidences. 8
- (d) Explain the term 'Stereochemical Control of Valence' with respect to nitrosyl complexes. Discuss the reaction of $[Ir(Co)Cl(PPh_3)_2]$ with nitrosonium tetrafluoroborate. 8
- (e) Draw the active site structure of Hemerythrin and illustrate its role in O_2 transport. 8

17. (a) Construct the Orgel diagram for $[Ni(NH_3)_6]^{2+}$ and hence assign the possible spectral transitions. 8
- (b) Discuss the nature of metal-metal bonds in $Cr_2(OAc)_4 \cdot 2H_2O$ by using suitable model. 8
- (c) Explain using suitable splitting diagrams, why $Cu(II)$ complexes are subject to tetragonal elongation rather than tetragonal compression. 8
- (d) Calculate the CFSE of the following complexes: 8
- (i) $[Cr(H_2O)_6]^{2+}$ 2x4=8
- (ii) $[Co(NH_3)_6]^{3+}$
- (iii) $[Fe(CN)_6]^{4-}$
- (iv) $[PtCl_6]^{2-}$
- (e) Discuss the role of NaKATPase in the transmission of nerve impulses across the membrane of cells. 8

Group - B

18. (a) Derive thermodynamically the Clausius Claperon equation for a liquid \rightleftharpoons vapour equilibrium, stating the assumption involved. 8
- (b) Show that if A undergoes simultaneous reactions $A \begin{matrix} \xrightarrow{k_1} B \\ \xrightarrow{k_2} C \end{matrix}$, then the activation energy ' E_a ' for the above reaction is $E_a = \frac{k_1 E_1 + k_2 E_2}{k_1 k_2}$
- where E_1, E_2 — activation energy of the two reactions. 6
- (c) State the differences between physical and chemical adsorption. Explain how the number of occupied sites (θ) can be calculated using Langmuir adsorption isotherm. 9
- (d) Derive the selection rule for a diatomic molecule undergoing rotational spectroscopy. 7
- (e) What do you mean by an azeotrope? Calculate the degree of freedom for an azeotrope in a two component liquid vapour equilibrium. 4
- (f) State Franck Condon principle. Mention its significance. 6
19. (a) Draw the concentration vs. time graph for three species A, B, C undergoing the following first order consecutive reaction
- $$A \rightarrow B \rightarrow C$$
- Explain the nature of the plot. 4
- (b) The reaction $2NO + O_2 \rightarrow 2NO_2$ follows the following pathway.
- $$2NO \rightleftharpoons N_2O_2 \text{ (Fast)}$$
- $$N_2O_2 + O_2 \rightarrow 2NO_2 \text{ (Slow)}$$
- Find the order of the reaction. 6

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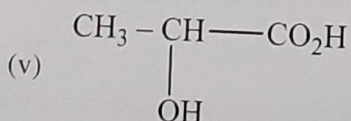
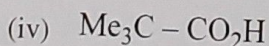
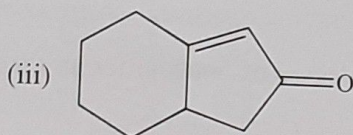
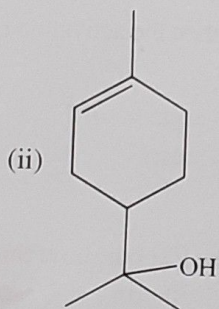
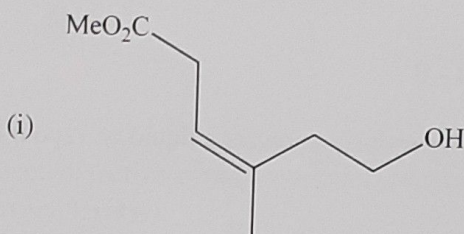
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- (c) State the differences between step growth and radical polymerization mechanism. Give an example of each type. 8
- (d) Derive the relation between elevation of boiling point of a solvent and molal concentration of the solution of a non-volatile, non electrolyte solute stating the assumptions and approximations. 8
- (e) Define a harmonic oscillator. Draw and explain the potential energy (v) versus displacement (x) curve of a harmonic oscillator. 5
- (f) State Lambert Beers Law explaining the terms involved. Explain its physical significance. 4
- (g) State with the characteristic energy profile, the basic assumptions of Transition State Theory. 5

Group - C

20. (a) Outline the synthetic route for each of the following compounds:

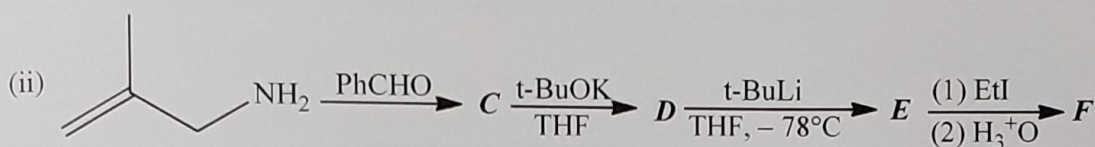
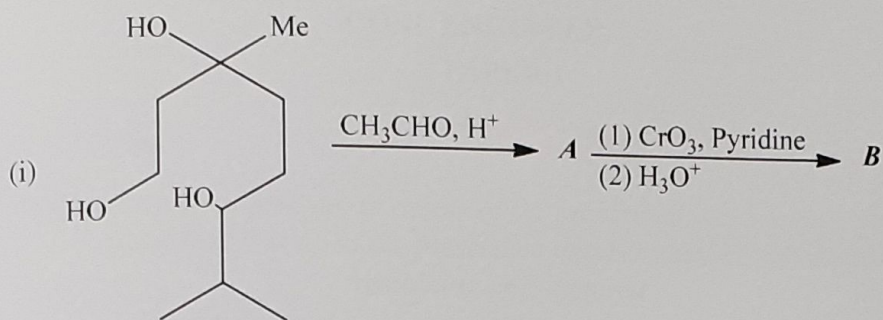
4x5=20



- (b) Draw the preferred conformer of 1-methyl-1-phenyl cyclohexane. Explain. 4
- (c) Identify the symmetry elements present in the following cases. Assign point group and symmetry number to each structure.
Allene, boat conformation of cyclohexane, *trans*-decalin, benzene. 4x4=16

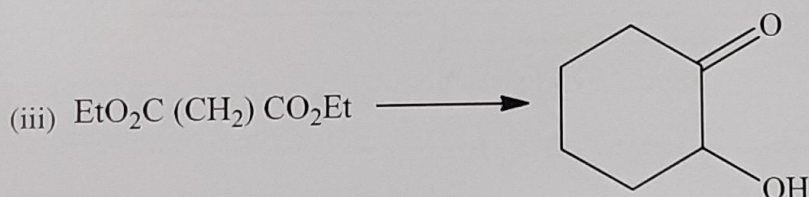
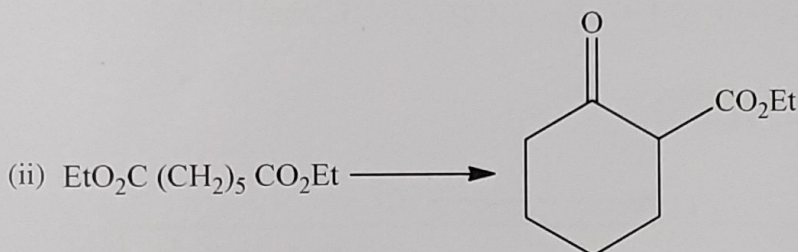
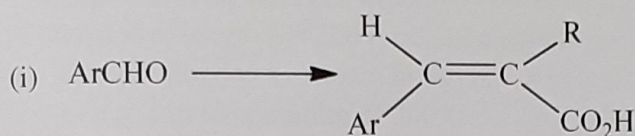
21. (a) Identify the products **A** – **F** of the following reactions:

1½×6=9



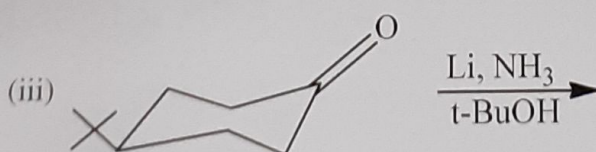
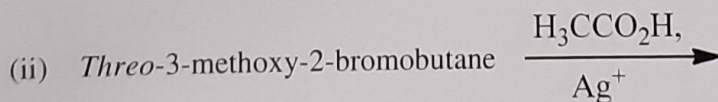
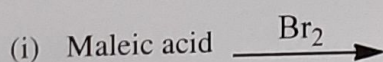
(b) Carry out the following conversions. Explain the reactions involved.

4×3=12



(c) Explain the stereochemistry of the following reactions. Indicate stereochemistry of the major products of each reaction.

5×3=15



(d) Find out the symmetry elements present in Twistane and point group.

4