BMW(O)-CH-II/21

2021

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

1. Using 18C rule as a guide, find the number(n) of carbonyl (CO) ligands in $[Co(\eta^5-C_5H_5)(CO)_n]$ and using the same rule establish the possible structure of $Co_4(CO)_{12}$. 2+2=4

2. What happens when $[V(CO)_6]$ and $[Mn_2(CO)_{10}]$ are separately reacted with metallic Na? 2+2=4

3. Cu(II) does not disproportionate whereas Au(II) disproportionates to Au(I) and Au(III). Explain. 4

4. Which organometallic compounds in sea water can methylate Hg(II) ions in sea water? Which natural product transfers its methyl group to Hg(II) in water? 1+3=4

5. Which compounds are called 'inverse spinels'? Cite one example. Why is this naming? 2+1+1=4

Group-B

6. Boiling points of aqueous solutions of 1 molal sucrose and 1 molal NaCl are different— Explain. 4

7. What is the essence of Franck-Condon principle? How is it reflected on the Jablonski diagram? 4

8. For homogeneous catalysis, rate of reaction increases linearly with concentration of the added catalyst. But it does not happen the same way during heterogeneous catalysis— Justify. 4

9. A first order reaction takes 20 minutes for 10% of the reactant to undergo the reaction. Calculate the time needed for 10% of the reactant to remain unreacted. 4

10. Bond length of a diatomic molecule is generally determined from rotational or microwave spectroscopy. However, the essential criterion for a molecule to be active to rotational spectroscopy is that the molecule must have permanent dipole moment. Then how can one determine the bond lengths of molecules like H_2, O_2 or N_2? 4

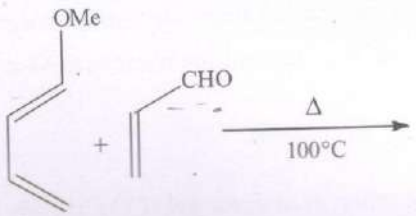
Group-C

11. Draw the conformers of 1-methyl-1-Phenylcyclohexane. Mention the isomeric relationship between them. Predict the most stable conformer. 4

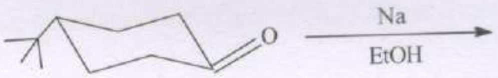
12. Draw the most stable conformetion of D–(+)-glucose. 4

13. Draw the preferred conformer of *cis*-cyclohexane-1, 3-di ol and explain with reason. 4

14. Write the product(s) of the following reaction. Comment on its formation. 4



15. Predict the product(s) of the following reaction with mechanism. 4



Section-II

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

Group-A

1. (a) Cite one example of a coordination compound,
   (i) which is thermodynamically stable but its exchange rate with its own ligand is very fast.
   (ii) which is thermodynamically stable but its exchange rate with its own ligand is very slow.
   (iii) Which is thermodynamically stable but its exchange rate with its own ligand is moderate
   1+1+1=

   (b) For high spin octahedral Co(II) complexes, the observed magnetic moments are higher tha the spin-only moment. Explain.

(c) Consider the following two reductive transformations:

$$SiCl_4 \longrightarrow SiH_4$$
$$GeCl_4 \longrightarrow GeH_4$$

Which transformation needs $LiAlH_4$ and which needs Zn/HCl? Explain. 2+2=4

(d) What is meant by 'Polytopal' isomers or 'Allogons'? Cite one example with only the outline of their conversions. 2+3=5

(e) A metal ion M^{2+} forms complexes of composition $M(en)_3^{2+}$, $M(H_2O)_6^{2+}$ and MBr_6^{4-} which are differently colored like blue, red and green, respectively. Identify which complex is green using CFT(en = ethylenediamine). 3

(f) Although aqueous solution of Fe(II) rapidly undergoes irreversible oxidation in air, the metalloprotein haemoglobin reversibly binds dioxygen (O_2) without being oxidised. Explain this fact. 6

(g) $Na_2[Fe(CO)_4]$ acts as a Grignard like reagent. Justify. What is the coordination geometry around the Fe^{2-} ion? 4+1=5

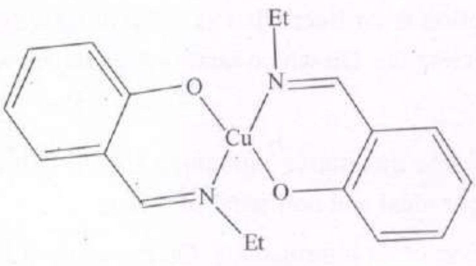
(h) While aqueous Fe(II) reacts with $EDTA^{4-}$ rapidly at normal laboratory temperature, aqueous Cr(III) reacts extremely slowly. Explain. 4

(i) Deoxyhaemoglobin is weaker Bronsted acid than oxyhaemoglobin. Explain this observation. 7

2. (a) Mo(v) is a $4d^1$ system. $(NH_4)_2[MoOCl_5]$ is paramagnetic ($\mu \approx 1{\cdot}73$ BM) whereas [Mo O_2Q Py] is diamagnetic (HQ is quinaldic acid). Mo O_2Q Py has pentavalent Mo. Generalise the magnetic data. 6

(b) Write a short explanatory note on 'Spin State Isomerism' with at least one typical example. 4

(c) Which of the two following Cu(II) complexes can be reduced more easily? 4



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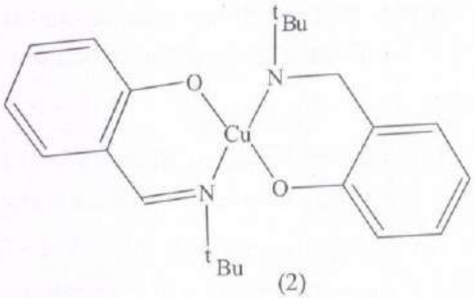


(2)

(d) Consider the lattice energies of the halides CaX_2 to ZnX_2 (X = F, Cl, Br or I). It is expected that a gradual increase in lattice energy should be observed from CaX_2 to ZnX_2 due to size factors of the cations. However, it is experimentally seen that the gradual increase is deviated in the regions of V^{2+} and Ni^{2+}. Explain this observation. 5

4\. (a) What are the differences between physisorption and chemisorption? Show that Langmuir adsorption isotherm in certain situation is converted to Freundlich adsorption isotherm. 3+7=10

(b) Use of catalyst can not shift the equilibrium of a chemical reaction. Still costly catalysts are used by the chemical companies. Explain the benefit of using a catalyst. 5

(c) Given the structure of linear CO_2 molecule how can you judge whether a typical mode of vibration will be IR active or inactive? Explain why it is essential to change the potential energy curve (PEC) for a stretching vibration from parabolic pattern to Morse potential energy pattern. On the same qualitative plot present a harmonic and an anharmonic (Morse) PEC. From the drawing how do you get the bond dissociation energy? 3+2+3+2=10

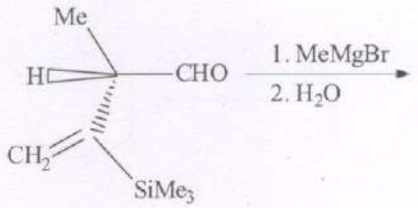
(d) What is an inhibitor? How does it work? 2+5=7

(e) Define fluorescence and phosphorescence. Singlet to Triplet or Triplet to Singlet radiative transition is forbidden. Still we observe phosphorescence— How? 4+4=8

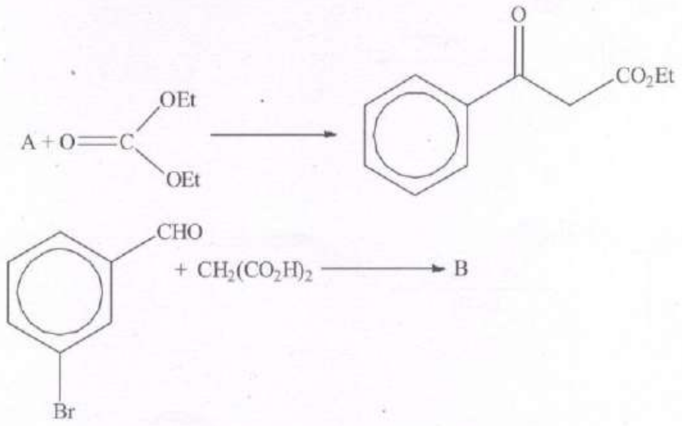
Group-C

5\. (a) Predict the possible stereoisomers of PhCH(OH)CH = CHMe. Assign their E/Z and R/S nomenclature. 10

(b) Determine the major and minor product obtained in the following reaction. Assign their stereoisomeric relationship. 10



(c) Identify "A" and "B" in the following reactions. Write the mechanism involved in the reactions. 10



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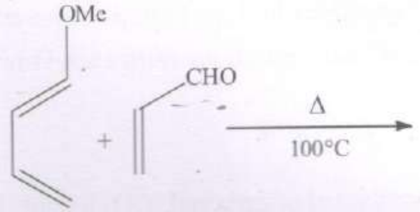

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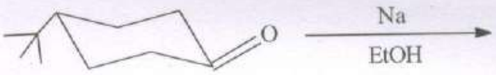

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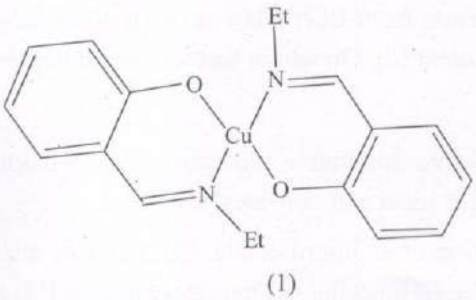

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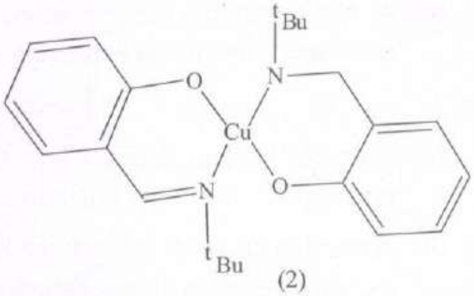

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(e) Comment on the origin of color and magnetic behaviour of hemerythrin in its oxygen bound state. 2+2=4

(f) Although oxygen is assumed to be a weak field ligand, how oxygen insertion to deoxy-haemoglobin results in the spin state change from high spin to low spin? 6

(g) Consider the three following reactions:

$$M + LL \rightleftharpoons M(LL)\ K_1$$
$$M(LL) + LL \rightleftharpoons M(LL)_2\ K_2$$
$$M(LL)_2 + LL \rightleftharpoons M(LL)_3\ K_3$$

where M is a transition metal ion, LL is bidentate ligand and K_1, K_2, K_3 are the stability constants respectively for the species M(LL), $M(LL)_2$ and $M(LL)_3$. Show that $K_1 : K_2 : K_3$ is $\frac{12}{1} : \frac{5}{2} : \frac{4}{15}$ 7

(h) For a d^3 system, show the possible three electronic transitions in the coordination system. 4

Group-B

3. (a) Knowing the cross sectional area of a single molecule of the adsorbed gas molecule and using the following BET equation how can you get the surface area of a solid catalyst (in powder form) per gram?

$$\frac{p}{v[p_0 - p]} = \frac{c-1}{v_m c}\left(\frac{p}{p_0}\right) + \frac{1}{v_m c}$$

Where v = volume of adsorbed gas

p = equilibrium pressure of adsorbate

p_0 = saturation pressure of adsorbate

c = BET constant

$v_m = v$ corresponding to a monlayer 9

(b) At higher solution concentrations deviation from Beer's law is often observed— justify or criticise. Define molar extinction coefficient (ε). On which factors does it depend? 3+2+4=9

(c) State and explain Raoult's law. On a same qualitative plot show the variation of vapour pressure as a function of mole fraction for ideal and non-ideal solutions. (2+3)+3=8

(d) A reaction proceeds through the formation of an intermediate. On the same qualitative plot show the variation of concentration of the (i) reactant, (ii) intermediate and (iii) product as a function of time. Justify your plot. 3+4=7

(e) What is meant by number average (M_N) and mass average molecular mass (M_W) of a polymer? Name one method each for the determination of the two types of molecular masses. Ideally when can you expect same value of the two molecular masses of a polymer? 3+2+2=7

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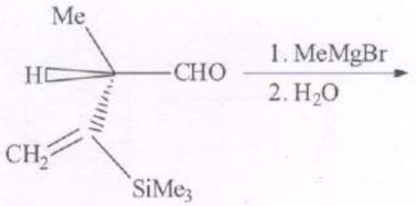

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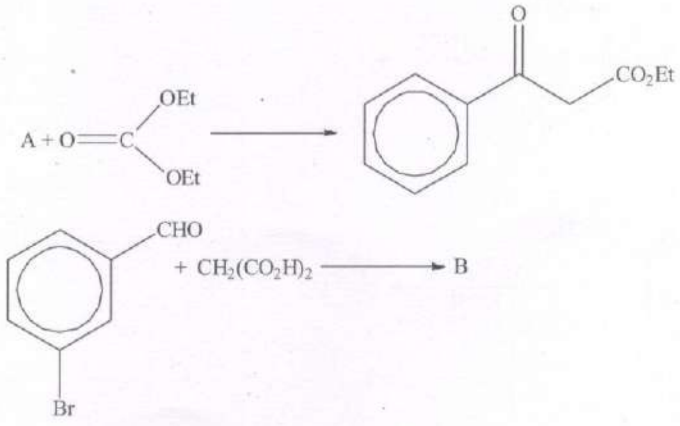
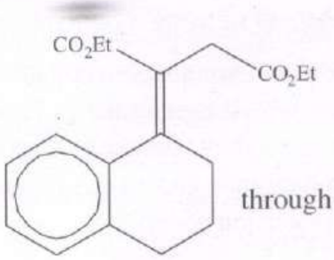


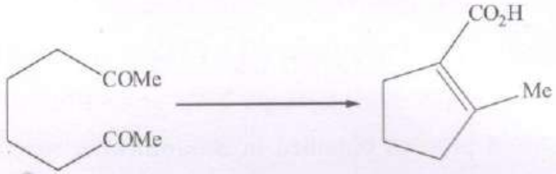
(d) Synthesize following compounds as directed.

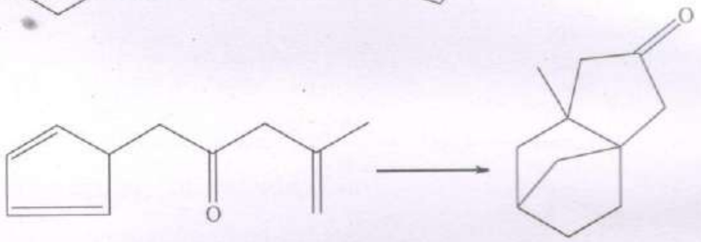
(i) $CH_3–CH=CH–CO_2H$ through Knoevenagel reaction

(ii)  through Stobbe condensation 10

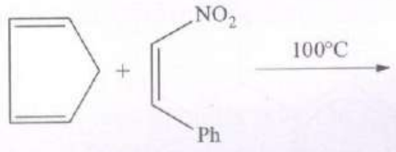
6. (a) Depict all possible stereoisomers of tartaric acid. Assign their stereoisomeric relationship and R/S notation. 10

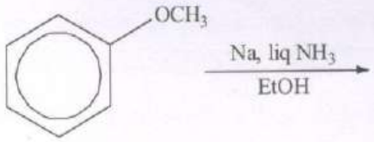
(b) Carry out following synthesis: 5×2=10

(i) 

(ii) 

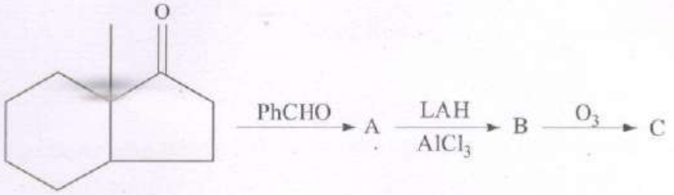
(c) Predict the following product(s) with mechanism: 5×2=10

(i) 

(ii) 

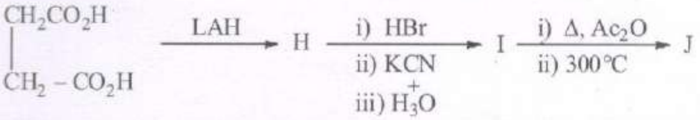
(d) Identify A – J: 1×10=10

(i)



(ii) $CH_3CO_2Et + (CH_2)_5(MgBr)_2 \xrightarrow{Et_2O} D \xrightarrow{-MgBr(OEt)} E \xrightarrow{H^+} F \xrightarrow[-H_2O]{H^+} G$

(iii)



$$\begin{array}{l} CH_2CO_2H \\ | \\ CH_2-CO_2H \end{array} \xrightarrow{LAH} H \xrightarrow[\substack{ii)\ KCN \\ iii)\ H_3\overset{+}{O}}]{i)\ HBr} I \xrightarrow[ii)\ 300°C]{i)\ \Delta,\ Ac_2O} J$$