

2022

CHEMISTRY — HONOURS

Paper : CC-8

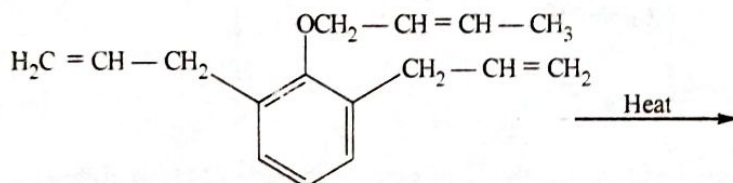
(Organic Chemistry - 4)

Full Marks : 50

*The figures in the margin indicate full marks.**Candidates are required to give their answers in their own words as far as practicable.*Answer *question no. 1* and *any eight* questions from the rest (*question no. 2 to 13*).1. Answer *any ten* questions :

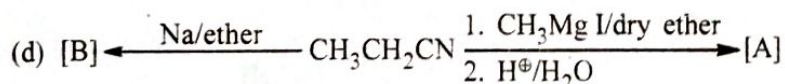
1×10

(a) Give the product(s) of the following reaction :



(b) The IR spectrum of benzene shows many peaks but its UV spectrum is very simple. Explain.

(c) Phenol is directly converted to anisole on reaction with diazomethane but an aluminium alkoxide catalyst is required to convert ethanol to ethyl methyl ether with the same reagent. Explain.



Give the structures of [A] and [B] (structures only).

(e) The difference in precessional frequency of a proton from TMS is 186 Hz in a 60 MHz NMR machine. Find its δ value.

(f) How do you protect propane-1,3-diol? Write down also the deprotecting agent.

(g) Explain why the normal isotope of carbon, ^{12}C is NMR inactive.

(h) Write down the products (only write down the structures of the products) obtained by diazocoupling of benzenediazonium chloride with alkaline 2-naphthol and aniline separately.

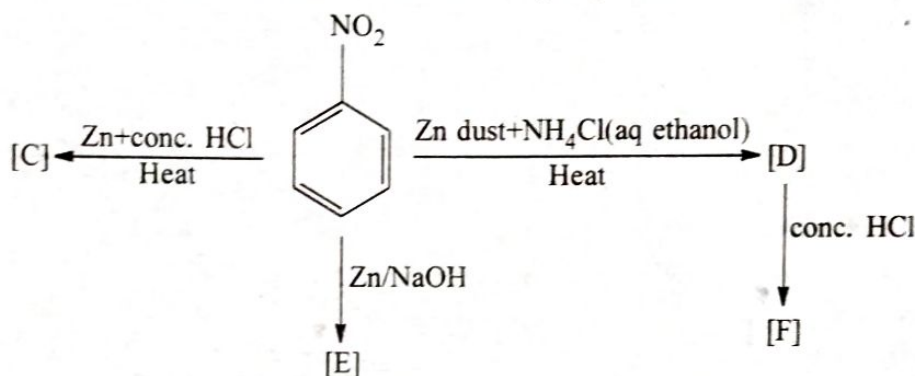
(i) Explain why *cis*- cinnamic acid absorbs at a higher frequency than its *trans*- isomer in the IR spectrum.(j) Give *one* example of each of the following :

(i) Illogical electrophile

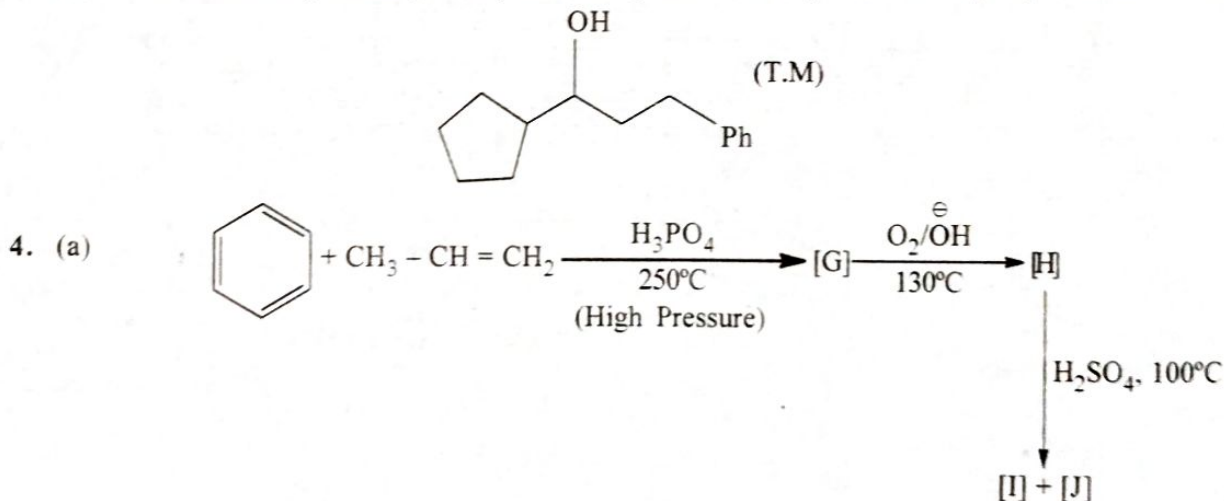
(ii) Illogical nucleophile

Please Turn Over

- (k) Write down the structures of the products when RCOOH and $\text{R}_2\text{C}=\text{O}$ are separately subjected to Schmidt reaction.
- (l) Write down the synthetic equivalents corresponding to the following synthons :
- (i) $\overset{\ominus}{\text{C}}\text{HO}$ (ii) $\overset{\ominus}{\text{C}}\text{Ph}$
2. (a) How is *threo* (active) isomer of butane-2,3-diol be distinguished from its *erythro* (*meso*) isomer by IR spectroscopy?
- (b) Explain why is tetramethylsilane (Me_4Si) (TMS) used as an internal standard in NMR spectral studies. Write down the unit used to measure coupling constant. 3+2
3. (a)

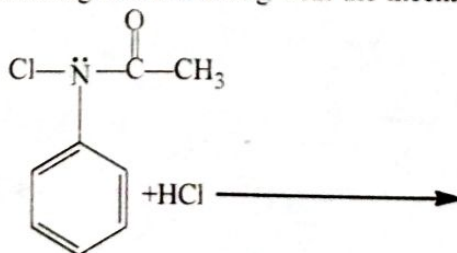


- (b) Show the retrosynthetic pathway and the synthesis of target molecule (TM) as follows : 3+2

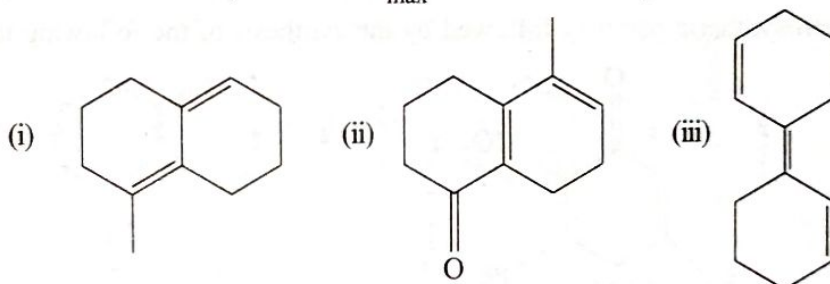


Give the structures of [G], [H], [I] and [J]. Show the mechanism involved in conversion of [H] to [I] and [J]

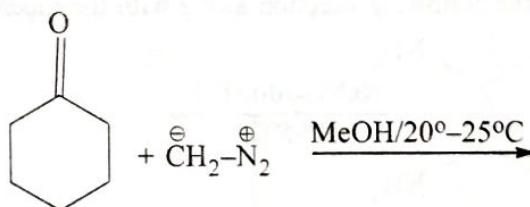
- (b) Give the product(s) of the following reaction along with the mechanism involved. 3+2



5. (a) Define stereospecific and stereoselective reactions and justify the difference between the two terms with the example of addition of singlet and triplet carbene to *Z*-2-butene.
- (b) Primary and secondary nitroalkanes can take part in Nef carbonyl synthesis, but tertiary nitroalkanes can not. Explain. 3+2
6. (a) Explain why anisole with a mixture of nitric and sulphuric acid gives *o*-nitroanisole in 31% yield whereas with $\text{HNO}_3 - \text{Ac}_2\text{O}$ gives the same product in 71% yield. Provide a suitable mechanism to justify the above observation.
- (b) Show how a single reagent can be used to distinguish between primary, secondary and tertiary aromatic amines (No mechanism is needed). 3+2
7. (a) Account for the following trends in λ_{max} (nm) : ethylene (175), 1,3-butadiene (217); and 1,3,5-hexatriene (250). Explain why 1,5-hexadiene ($\lambda_{\text{max}} = 185$ nm) does not absorb light above 200 nm.
- (b) Discuss the difficulties of synthesising $\text{Me}_3\text{C} - \text{NH}_2$ by Gabriel phthalimide synthesis. Show how Me_3CNH_2 can be prepared from $\text{Me}_3\text{C} - \text{OH}$. 3+2
8. (a) Using Woodward-Fieser rule, calculate λ_{max} of the UV absorption for the following compounds :

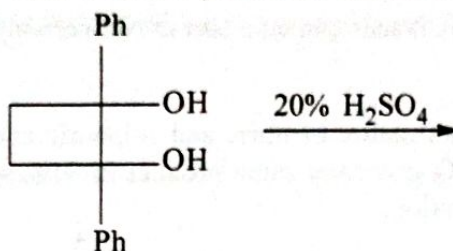


- (b) Give the product(s) of the following reaction along with the mechanism involved. 3+2

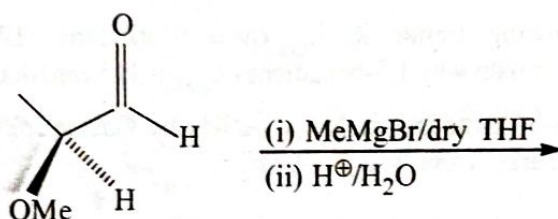


9. (a) An organic compound with molecular formula $\text{C}_6\text{H}_{12}\text{O}$ gives positive iodoform test. Its IR and ^1H NMR spectral data are as follows.
- IR : $\nu_{\text{cm}^{-1}} = 1710 \text{ cm}^{-1}$ (strong)
- ^1H NMR : $\delta_{2.1}$ (3H, s) and 1.1 (9H, s).
(ppm)
- Deduce the structure of the molecule with proper justification.
- (b) What is the range of 'finger print region' in IR spectroscopy in cm^{-1} ? Justify the naming of this range. 3+2

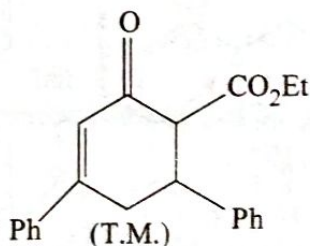
10. (a) The following reaction gives a single product. Give the structure of the product and also explain mechanistically why the other isomeric product is not formed.



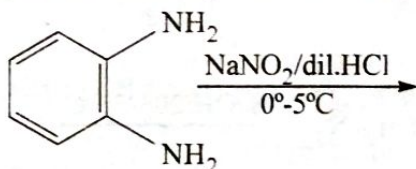
- (b) Use Felkin-Anh's model to determine the stereochemistry of the major product of the following reaction : 3+2



11. (a) Give the retrosynthetic pathway followed by the synthesis of the following target molecule (TM) :



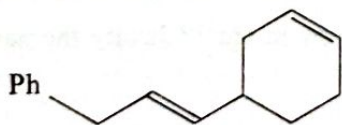
- (b) Give the product(s) of the following reaction along with the mechanism involved : 3+2



12. (a)
$$\text{Ph}_2\text{C}(\text{OH})_2 - \text{CMe}_2 + \text{Ph}_2\text{C}(\text{OH})_2 - \text{CEt}_2 \xrightarrow{\text{H}^+} [\text{K}] + [\text{L}]$$
- (I) (II)

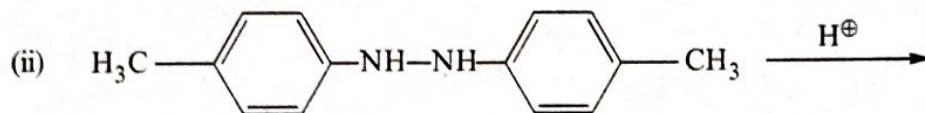
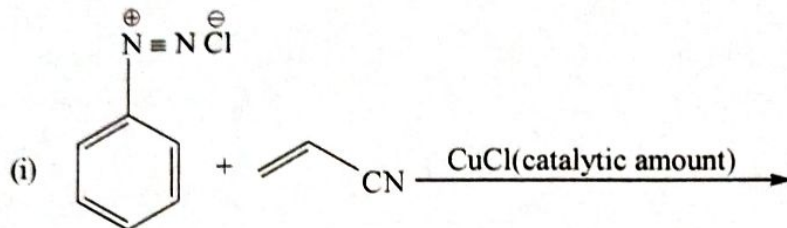
Explain the products of the reaction mechanistically.

- (b) Give possible modes of retrosynthetic analysis and efficient synthesis for



Which mode is better choice?

13. (a) Give the products of the following reactions along with plausible mechanism :



(b) Define the terms 'chemically equivalent' and 'magnetically equivalent' used in ^1H NMR spectroscopy. Give an example of a molecule with chemically equivalent but magnetically non-equivalent protons with proper justification. 3+2

2022

CHEMISTRY — HONOURS

Paper : CC-9

(Physical Chemistry-3)

Full Marks : 50

*The figures in the margin indicate full marks.**Candidates are required to give their answers in their own words as far as practicable.*Answer **question no. 1** and **any eight** questions from the rest.1. Answer **any ten** questions :

1×10

- What is the essential weakness of the Debye Theory of heat capacity of crystals?
 - How many octahedral and tetrahedral holes are possible in a fcc structure?
 - A powder diffraction photograph from a metal (M) shows lines, which shows indices as (110), (200), (211), (220), (310), (222), (321), (400)...
- Identify, what the symmetry of the unit cell should be.
- Using Einstein's heat capacity of solid, obtain the Dulong-Petit's Law.
 - What is the relation between $\bar{1}1$ and $1\bar{1}$ planes of a square lattice?
 - Calculate and explain the number of components of phenol-10% NaCl aqueous solution system, pertaining to the determination of the consolute temperature.
 - Does Compton shift depend on the material of the scattering? Justify your answer.
 - Show $(\hat{A}^\dagger)^\dagger = \hat{A}$.
 - What is the essence of the superposition of states in quantum mechanics?
 - Fusion mixture is used in quantitative analysis for fusion. — Why? (Answer in the light of phase rule)
 - Check the acceptability of $\psi = e^{-x^2}$ in the range $(-\infty, +\infty)$.
 - Prove that if $\psi(x)$ is a solution to the Schrödinger equation, then any constant times $\psi(x)$ is also a solution.

- Derive Duhem-Margules equation and show that if one component obeys Raoult's Law, then the other will also obey.
- What do you mean by phase transition of first order? Show using diagram how C_p changes with temperature (T).

3+2

Please Turn Over

3. (a) State with reasons the degrees of freedom (F) inside the bound area, outside the bound area and at the critical solution temperature for phenol-water system.
- (b) Calculate the osmotic pressure at 300K of a solution formed by dissolving 1 gm of glucose and 1 gm of sucrose in 1 litre of water. 3+2
4. (a) 0.01 M acetic acid aqueous solution shows depression of freezing point by 0.0194°C while 0.01 M solution in benzene shows the depression by 0.0216°C . Given $K_f = 5.12 \text{ kg mol}^{-1}$ for benzene. Predict the state of acetic acid in these two solutions.
- (b) If ψ_1, ψ_2 (orthonormal) be the eigenfunctions of a Hermitian operator \hat{A} with eigenvalues a_1 and a_2 respectively, then the linear combination $(c_1\psi_1 + c_2\psi_2)$ is not necessarily an eigenvalue of \hat{A} . Then what is the expectation value of \hat{A} ? 3+2
5. (a) Find the simplest formula of a solid containing 'X' and 'Y' atoms in a cubic arrangement in which 'X' atoms occupy the corners and 'Y' atoms occupy the centres of the faces of the unit cell. If the side of the unit cell is 50 nm, estimate the density of the solid assuming atomic masses of 'X' and 'Y' to be 60 and 90 respectively.
- (b) State with reason if the following function is acceptable :
- $$\psi(x) = \sin^{-1} x \left[\text{where, } (-1 \leq x \leq 1) \text{ and } \left(-\frac{\pi}{2} \leq \psi(x) \leq \frac{\pi}{2} \right) \right] \quad \text{3+2}$$
6. (a) Prove that any operator defined as product of two non-commuting operators is not Hermitian even if when the operators themselves are hermitian. How will you make the operator hermitian in this case?
- (b) What is the consequence if two operators do not commute? 3+2
7. (a) For a two component solutions (say, A and B) that obeys Raoult's Law, vapour pressure problems involve as many as four mole-fractions and five vapour pressures. Obviously, we have five unknown pressures, two unknown independent mole-fractions. To solve the problem, explain at least how many pieces of information you require to solve the problem.
- (b) If two operators \hat{A} and \hat{B} commute, then show that they have the same set of eigenfunctions, ψ_i (where $i = 1, 2, 3, \dots$) 3+2
8. (a) Show that for ideal solution, $\Delta H_{\text{solution}} = 0$.
- (b) (i) How did Debye modify the Einstein theory of heat capacity of monatomic crystal?
- (ii) Draw the curves that show the plots of frequency distribution of normal modes in a crystal for both the Einstein and the Debye theories. 2+3

9. (a) The energy state of a particle in a cubicle box ($V = 0$) is $\frac{38h^2}{8ma^2}$. State the degrees of degeneracy and assign the states.
- (b) Prove that if $\hat{\alpha}$ and $\hat{\beta}$ are two linear operators, then $(\hat{\alpha} + \hat{\beta})$ and $(\hat{\alpha}\hat{\beta})$ are also linear operators. 3+2
10. (a) Why is x-ray used to get diffraction pattern of a solid? Can we use electron beam for the same?
- (b) The (2 2 2) planes of cubic tantalum unit cell gives a reflection at $21^\circ 5'$ for $\lambda = 0.71 \text{ \AA}$. What is its edge length? 2+3
11. (a) In CaF_2 crystal, Ca^{+2} is arranged in a fcc type crystal structure, while the fluoride ions occupy all the tetrahedral holes. Justify the formula of CaF_2 .
- (b) Verify that the wave functions of a particle in a one-dimensional box of width 'a' and infinite height are orthogonal. 3+2
12. (a) Derive the Nernst Distribution Law using the concept of chemical potential.
- (b) A certain mass of substance when dissolved in 100 gm of Benzene, lowers the freezing point by 13°C , which when dissolved in water, the same mass lowers the freezing point by 14°C . If the substance has a normal molecular weight in benzene and in water it is completely dissociated, how many ions in water does it dissociate into? 3+2
13. (a) How would you distinguish an azeotrope from a compound?— Give an argument only. What is the degree of freedom of an azeotrope (of a binary liquid)?
- (b) Show that $\langle x \rangle = \frac{a}{2}$ for all the states of a particle in a box, where 'a' is the length of the box. Is this result physically reasonable? 2+3
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2022

CHEMISTRY — HONOURS

Paper : CC-10

(Inorganic Chemistry)

Full Marks : 50

*The figures in the margin indicate full marks.**Candidates are required to give their answers in their own words as far as practicable.*

Answer question no. 1 and any eight questions from the rest.

1. Answer any ten questions :

.1×10

- Find out the electronic state of an ion with 3F_4 ground term.
- Cite an example of tetragonally compressed molecule.
- What would be spin only magnetic moment of Mn^{3+} in $[Mn(H_2O)_6]Cl_3$?
- Show the Scheme of preparation of *cis*- $PtCl_2(C_2H_4)(NH_3)$ from $[PtCl_4]^{2-}$.
- Account for the dark red colour of $[Fe(bipy)_3]^{2+}$ (bipy = bipyridine).
- Identify the metal ion(s) able to show Jahn-Teller effect in their high spin state :
Cr(II), Fe(II), Ni(II), Mn(IV), Mn(III)
- Identify the transition(s) which are not allowed according to selection rule :
 $2s \rightarrow 2p$, $3p \rightarrow 3d$, $2s \rightarrow 3p$, $3s \rightarrow 3d$, $1s \rightarrow 2s$.
- Find out the number of unpaired electron(s) in Gd ($z = 64$).
- Arrange the following ligands in a spectrochemical series : H_2O , NH_3 , F^- , OH^- , CN^- , CO
- State ground state term for Fe^{2+} .
- Mention the M^{2+} ion in 3d-transition series, that possesses minimum ionic radius value in low spin state.
- Give the structure of the complex 'A'. $[Pt(Cl)_3(NO_2)]^{2-} \xrightarrow{NO_2^-} A$.

2. (a) Using Orgel diagram, explain the possible transitions of $[Cr(H_2O)_6]^{3+}$ complex. Which transition corresponds to 10 Dq value?(b) Explain the order of LMCT transition energies : $MnO_4^- < TeO_4^- < ReO_4^-$.

3+2

Please Turn Over

3. (a) Pd(II) and Pt(II) form square planar complexes exclusively but Ni(II) forms square planar complexes under certain condition. Explain.
- (b) Δ_o for three hexaamines differs as follows :
- $$[\text{Co}(\text{NH}_3)_6]^{3+} = 23000 \text{ cm}^{-1}$$
- $$[\text{Rh}(\text{NH}_3)_6]^{3+} = 34000 \text{ cm}^{-1}$$
- $$[\text{Ir}(\text{NH}_3)_6]^{3+} = 41000 \text{ cm}^{-1}$$
- Identify the factor(s) involved for this difference. 3+2
4. (a) $10 Dq$ for $[\text{Mn}(\text{H}_2\text{O})_6]^{3+}$ is known from electronic spectrum as 21000 cm^{-1} . The pairing energy of Mn(III) is 28800 cm^{-1} . Predict whether the complex is high spin or low spin and also calculate the CFSE value.
- (b) Cr(II) acetate monohydrate is diamagnetic. Explain. 3+2
5. (a) How will you separate lanthanides using ion-exchange methodology?
- (b) Estimation of activation energy for aquation reaction of octahedral Co(III) and Cr(III) complexes indicates that a pentagonal bipyramid intermediate path is followed by Cr(III), while for Co(III) the intermediate is a square pyramid. Comment on their mechanistic path. 3+2
6. (a) Addition of concentrated HCl to pale pink $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ changes its colour to blue but similar addition to $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ has no effect. Justify this from the point of OSSE.
- (b) Explain the exceptional stability of +2 oxidation state of Eu ($z = 63$) and Yb ($z = 70$). 3+2
7. (a) Lanthanides show poor tendency to form complexes with π acid ligands while the same is greater for actinides. Explain.
- (b) In high spin octahedral and tetrahedral complexes of Co(II) three unpaired electrons are present; but magnetic moment for the octahedral complexes are 4.8-5.2 BM whereas for tetrahedral it is 4.2-4.8 BM.— Explain. 3+2
8. (a) Explain mechanistically the high substitution rate for square planar platinum (II) complexes in presence of a π -acid ligand.
- (b) Between two redox couples, $[\text{Co}(\text{NH}_3)_6]^{3+}/[\text{Co}(\text{NH}_3)_6]^{2+}$ and $[\text{Co}(\text{H}_2\text{O})_6]^{3+}/[\text{Co}(\text{H}_2\text{O})_6]^{2+}$, which one is more oxidizing and why? Explain on the basis of CFT. 3+2
9. (a) Actinides show variety of oxidation states while lanthanides exhibit uniform (+3) oxidation state. Why is it so?
- (b) Fe^{3+} (aq) reacts rapidly with EDTA at room temperature, while Cr^{3+} (aq) reacts slowly. Comment. 3+2
10. (a) What is lanthanide contraction? Explain why Zr and Hf have similar properties although they belong to different periods.
- (b) Explain the variation of hydration energy of M^{2+} ion in 3d transition series. 3+2

11. (a) Both the metal ions in $K_3[CuF_6]$ and $K[AgF_4]$ possess d^8 electronic configuration but one is paramagnetic and the other is diamagnetic. Identify them with justification.
- (b) Predict the colour of the complex $[Ti(H_2O)_6]^{3+}$ [Given $\Delta_o = 20,000 \text{ cm}^{-1}$]. 3+2
12. (a) Explain the abrupt drop of $\log k_3$ value in the complexation of $[Cu(H_2O)_6]^{2+}$ with ethylenediamine at 30°C .
- $[Cu(H_2O)_6]^{2+} + en \rightleftharpoons [Cu(H_2O)_4en]^{2+} + 2H_2O \quad \log k_1 = 10.72$
- $[Cu(H_2O)_4en]^{2+} + en \rightleftharpoons [Cu(H_2O)_2(en)_2]^{2+} + 2H_2O \quad \log k_2 = 9.31$
- $[Cu(H_2O)_2(en)_2]^{2+} + en \rightleftharpoons [Cu(en)_3]^{2+} + 2H_2O \quad \log k_3 = -0.90$
- (b) Establish the structure of $NiFe_2O_4$ and Mn_3O_4 as normal or inverse spinel. 3+2
13. (a) Justify the distorted octahedral structure of $[Cu(H_2O)_6](ClO_4)_2$
- (b) Explain antiferromagnetism through superexchange using a suitable example. 3+2
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2022

CHEMISTRY — HONOURS

Paper : SEC-B-4

(Pesticide Chemistry)

Full Marks : 80

The figures in the margin indicate full marks.

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

Answer *question no. 1* and *any twelve* questions from the rest (*question nos. 2 to 14*)

1. Answer *any twenty* questions :

1×20

- (a) What is a herbicide?
- (b) Give two examples of botanical pesticides.
- (c) Write down the full form of 'SAR' in pesticide chemistry.
- (d) Give two examples of pathogens which causes plant disease.
- (e) The book 'Silent Spring' is written by_____.
- (f) Name two inorganic pesticides.
- (g) What does the term γ suggest in the name γ -HCH?
- (h) Insecticides generally attack_____system.
- (i) What happens when chloranil is exposed in presence of sunlight and moisture?
- (j) Cite one example of a rice herbicide.
- (k) Write the name of a carbamate insecticide which is marketed under the trade name of 'Furadan'.
- (l) Mention any two uses of carbofuran.
- (m) Which of the following is not an aryl phosphate?
 - (i) TIK 20
 - (ii) Malathion
 - (iii) Parathion
 - (iv) Folidol.
- (n) Baygon contains (write down the proper answer)
 - (i) Malathion
 - (ii) Propoxur
 - (iii) Carbofuran
 - (iv) Aldicarb.
- (o) Organophosphates inhibit
 - (i) Enterokinase
 - (ii) Urease
 - (iii) Cholinesterase
 - (iv) Carbohydrase.

Please Turn Over

- (p) Which of the following is not a pesticide?
- (i) Chloropicrin (ii) Malachite green
(iii) Fluoroacetamide (iv) Nicotine.
- (q) Give one reason of toxicity of DDT.
- (r) What is BHC?
- (s) What is the effect of γ -hexachlorocyclohexane on human health?
- (t) What is carbaryl?
- (u) What is parathion?
- (v) Give one example of a quinone pesticide with structure.
- (w) Name one pesticide which has furan ring. Give the structure.
- (x) Name one pesticide having anilide functionality and draw the structure.
2. (a) How do pests and pathogens damage the host plant?
(b) What are pests? 3+2
3. (a) Biopesticides are more useful than the chemical pesticides. Explain.
(b) What do you mean by biopesticide? Give one example. 3+2
4. (a) Mention three primary benefits of use of pesticides.
(b) Outline the environmental impacts of using pesticides. 3+2
5. (a) Write down the chemical reactions and conditions involved in the synthesis of gammaxene.
(b) Briefly discuss the mode of action of gammaxene. 3+2
6. (a) What is thiolo effect? Explain it.
(b) What are the special features of organophosphates? 3+2
7. (a) Write a short note on 'mode of action of malathion'.
(b) Briefly describe the chemical synthesis of malathion. 3+2
8. (a) Outline the similarity and difference between organophosphorus and carbamates with respect to mode of action.
(b) What are carbamates? Write down the general structural formula of carbamates. 3+2
9. (a) Mention the uses and side effects of carbaryl.
(b) Write down the structure of carbaryl and its hydrolysed products. 3+2
10. (a) Provide the names of two herbicides from the chloroacetanilide family. Draw their structures.
(b) How many isomers are possible for HCH? Which isomer is known as Lindane? 3+2

(3)

X(4th Sm.)-Chemistry-II/(SEC-B-4)/CBCS

11. (a) What are changing concepts of pesticides?
(b) How do pyrethrin and azadirachtin act? 3+2
12. (a) Discuss the harmful effects of Butachlor.
(b) Write down the preparation of Butachlor. 3+2
13. (a) How would you synthesise carbaryl from 1-naphthol? Write down the chemical reaction involved in the synthesis.
(b) What is fungitoxicity? Write down the name and structure of one fungitoxic agent. 3+2
14. (a) Mention the uses and side effects of carbofuran.
(b) What do you mean by 'integrated pest management'? 3+2
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