2016

M.Sc. Part–II Examination

CHEMISTRY

PAPER—VI

Full Marks : 75 / 100

Time : 3 / 4 Hours

The figures in the margin indicate full marks.

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

Illustrate the answers wherever necessary.

(*Physical Special*)

Old Syllabus

F.M. – 75   Time : 3 Hrs.

Answer any *five* questions
taking at least *two* from each group (A and B).

New Syllabus

F.M. – 100   Time : 4 Hrs.

Answer any *five* questions
taking at least *two* from each group (A and B) and
answer any *five* questions from group C.

(Turn Over)

Group—A

1. (a) Obtain the Sackur-Tetrode equation for molar translational entropy of a monatomic gas. 8

   (b) Calculate the molar rotational energy of F_2 at 300K.
   [Given $I = 32.5 \times 10^{-40}$ gcm^2, $k = 1.38 \times 10^{-22}$ JK^{-1},
   $h = 6.62 \times 10^{-34}$ JS] 7

2. (a) Derive the relationship between the Lagrangian multipliers α and β in terms of chemical potential. 3

   (b) Define the term grand partition function Z, obtain the expression for lnZ for bosons and derive the Bose-Einstein distribution law. 2+3+7

3. (a) What are meant by forces and fluxes in irreversible processes ? Write the equations of motion for a two-force two-flux process and state the Onsager reciprocity relation. What is its significance ? 2+2+2

   (b) Explain what is meant by entropy production ? Obtain the expression for entropy production for the flow of matter. 3+6

4. (a) Define ensemble average and time average in statistical mechanics and state the Ergodic hypothesis. 2+2+1

   (b) Obtain the expression for the rate of entropy production for a process involving two portions which differ with respect to pressure and electrical potential and write the appropriate phenomenological equation and with its helf define the phenomenon electroosmotic pressure in terms of the phenomenological coefficient. 5+2+3

5. (a) What is Mossbauer effect ? 3

   (b) Explain — (i) isomer shift (ii) quadrupole splitting. 3+3

   (c) How is Mossbauer effect related with resonance fluoresence ? 3

   (d) Discuss some applications of Mossbauer spectrocopy. 3

Group—B

6. (a) Define the terms — Relative viscosity, Reduced Viscosity and Intrinsic viscosity. 2

(b) A sample of γ-globulin gives the following experimental results at 20°C. –Specific volume of solute 0.718 mL g^{-1} density of the solvent 1.00 g/mL. Sedimentation coefficient 7.12×10^{-13}s, diffusion coefficient 4.0×10^{-11} m^{2}s^{-1}. Calculate the moss of γ-globulin.   3

(c) Derive Flory-Hugrins equation.   10

7. (a) Give significance of Activation energy.   3

(b) Establish the relation

$$K = \frac{k_B T}{h} \cdot e \cdot e^{A^* S^0 / R} \cdot e^{-Ea/RT}$$

where the symbols indicate usual meaning.   6

(c) For a bimolecular reaction, using partition function prove that, the expression of pre-exponantial factorise (P) is

$$P = \left(\frac{RT}{h}\right)\left(\frac{q_e / v}{q_{A/u}.q_{B/u}}\right).$$
    6

8. (a) Using double sphere activated complex model for ionic reaction, derive expression for rate constant in presence of solvent dielectric constant.   5

(b) Give difference between macroscopically diffusion control and microscopically diffusion control reaction.   3

(c) For full microscopic diffusion controlled reactions between two uncharged molecules A and B, find concentration of B molecule and rate of diffusion of B molecule (I_B) through its surface.   7

9. (a) Applying absolute reaction rate theory for viscosity show that

$$\eta = \frac{N}{V}(2\pi m k_B T)^{\frac{1}{2}} \cdot V_f^{\frac{1}{3}} \cdot e^{\epsilon_0 / k_B T}$$

where the terms have their usual meaning.   12

(b) Write short note on — Potential energy surface (PES).   3

Group—C

10. Answer any *five* questions :   5×5

(a) What is transmission coefficient ?   5

(b) What is molecular partition function ?   5

(c) For partial microscopic diffusion controlled reaction at hwat condition $k = K_{chem}$?   5

(d) In a particular sample of a polymer, 100 molecules have molecular weight 10^3 each, 200 molecules have molecular weight 10^5 each. Calculate number average and weight average molecular weight.   5

(e) What is the principle of equal a priori probability?   5

(f) State the condition for statistical equilibrium.   5

(g) State the principle of microscopic reversibility.   5

___
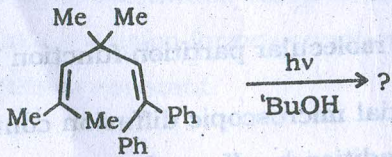
(Organic Special)

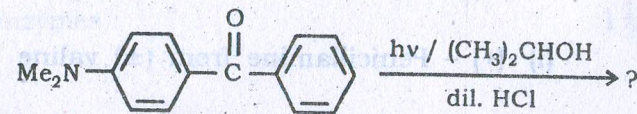### New Syllabus

F.M. – 100   Time : 4 Hrs.

Answer any *five* questions taking at least *two* from group A and B and group C is compulsory.

Group — A

1. (a) What is di-π-methane rearrangement? Explain the formation of product(s) mechanistically.   2+3

(b) (i) Predict the product for the following :

Quartum yield for this reaction is $\phi = 0.4$. Explain the observation.   3

(ii)
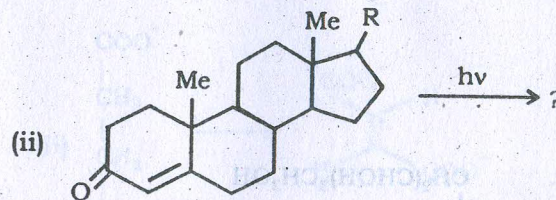
(c) What are Paterno-Buchii reaction? Discuss its mechanism with stereochemical consequences.

2+3

2. (a) What are the function of vitamin A and K.   2

(b) Write down the chemical structure of Vitamin B_1 and Vitamin C.   2

(c) Write all the steps for the synthesis of the following compounds : 3+4+4

(i) (+) – Penicillamine from (±) valine

(ii)

from

(iii)

from
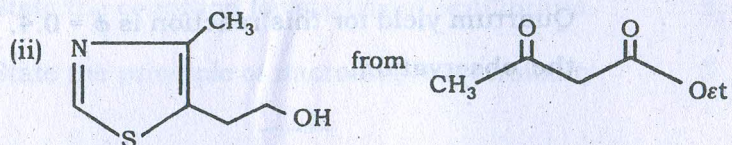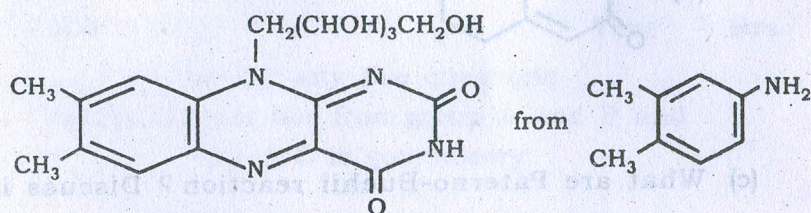
3. (a) Show how coenzyme of Vitamin B_1 takes part in decarboxylation of pyruvic acid, the end product of carbohydrate metabolism and depict the chemical reactions involved there in. 4

(b) Carry out the following transformations using enzymes / coenzymes : $1\frac{1}{2}\times2$

(i) $CH_3 - \overset{O}{\underset{||}{C}} - COO^- \longrightarrow CH_3 - \overset{OH}{\underset{|}{CH}} - COO^-$

(ii)
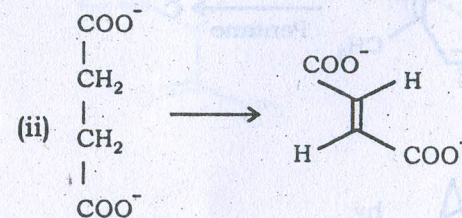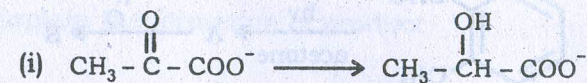
(c) Discuss the mode of action of the following coenzymes derived from various vitamins (with mechanism) :

(i) Coenzyme derived from Thiamine

(ii) Coenzymes derived from Riboflavin.

4+4

4. (a) Complete the following tranformations : 1×7

(i)

$\xrightarrow[\text{acetone}]{h\nu}$ A $\longrightarrow$ B

(ii)

$\xrightarrow[\text{Pentane}]{h\nu}$ C

(iii)

$\xrightarrow{h\nu}$ D
C_6H_6

(iv)

$\xrightarrow[\text{Cyclohexane}]{h\nu}$ E

(v)

$+$ $\xrightarrow[-78°c]{h\nu}$ F + G
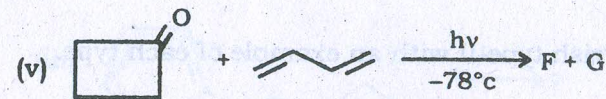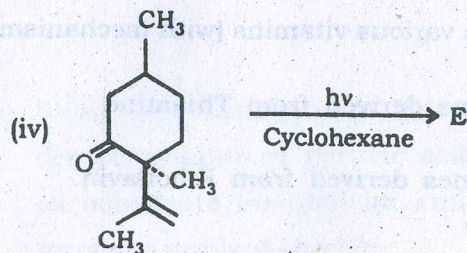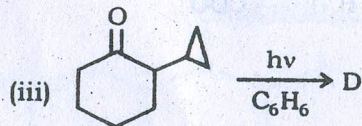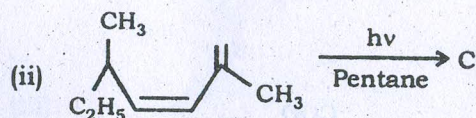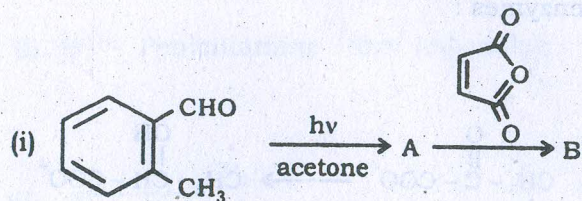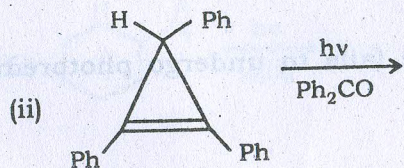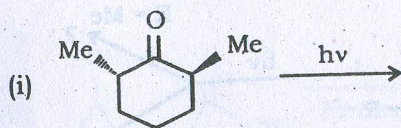
(b) Explain the formation of product 2+2

R = Me ?

R = H ?
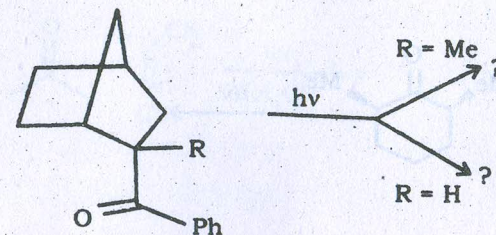
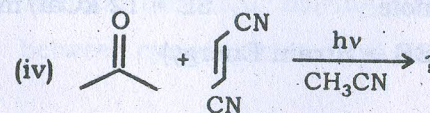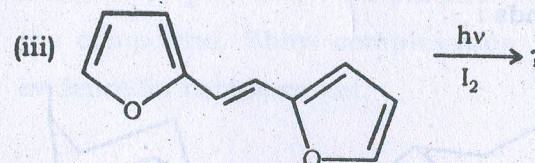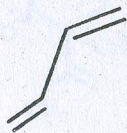(c) 2-Acetonapthone fails to undergo photoreduction reaction. 2

(d) Predict the product for following reaction : 2

$+$ $\xrightarrow{h\nu}$?
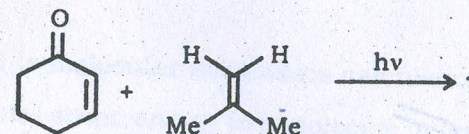
5. (a) Compare the reactions between Norrish type-I and Norrish type-II with an example of each type. $2\frac{1}{2}$

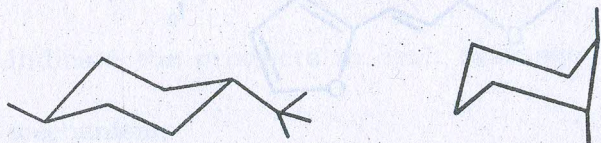(b) Indicate the products in each case with plausible mechanism. $5 \times 2\frac{1}{2}$

(i)

(ii)

Or

(iii)

(iv)

(v)
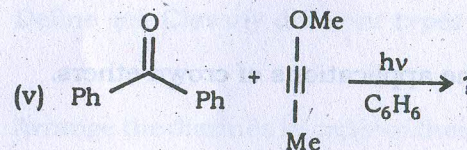
Group — B

6. (a) What is molecular mechanics calculation ? Write down the total strain energy of a molecule in terms of potential energy functions. 2+2

(b) Calculate the heat of formation of the following compounds :

S.E = 6.3 kCal/mole   SE = 12 kCal/mole

(SE → Strain Energy)   2+2

(c) Write the significance of multiple recognition sites in the selection of substral during host-guest complexation.

4

(d) Write down the applications of crown ethers.   3

7. (a) Write short note on : (any *two*)   2×4

(i) Rotaxane

(ii) Coenzymes and Cofactors

(iii) Hydrophobic effect

(iv) Van der waal interaction.

(b) Design a receptor for the complexation of urea. Synthesize the compound. Show complexation with urea. Give evidence for complexation.   1+2+2+2

8. (a) What is Cyclodextrine ? Provide the name of different compounds which form complex with cyclodextrine. Mention the major driving forces for the complexation between cyclodextrines and guest molecules.   2+2+2

(b) Define cryptands. How can cryptands be used for light conversion devices ?   2+3

(c) Define gel. Classify different types of gel.   2+2
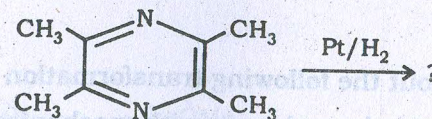
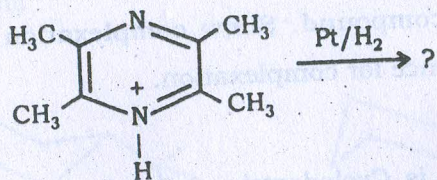9. (a) Arrange the diazines in order of their decreasing basicities and give explanation for each case.   2

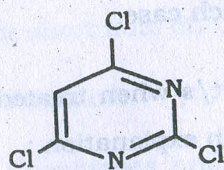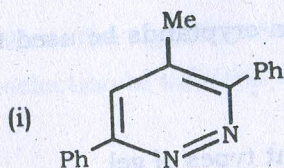(b) What would be the product/s when treated as follows and indicate the reason with explanation :   2

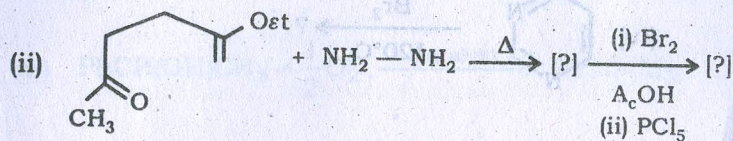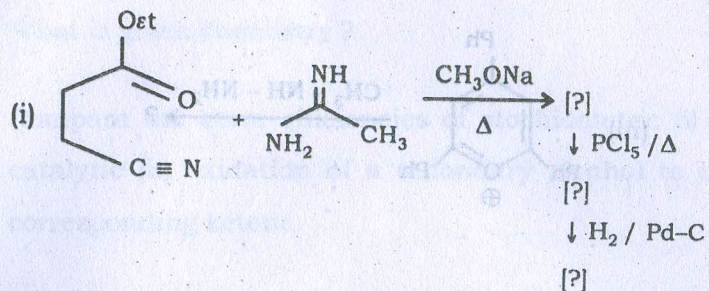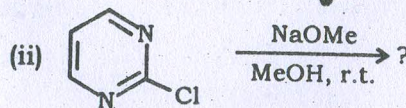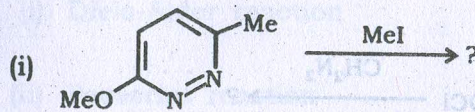$$CH_3 \quad \xrightarrow{Pt/H_2} \quad ?$$

$\xrightarrow{\text{Pt/H}_2}$?

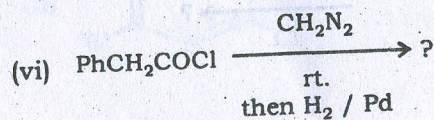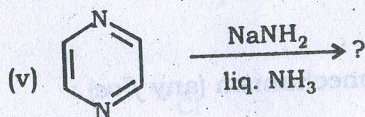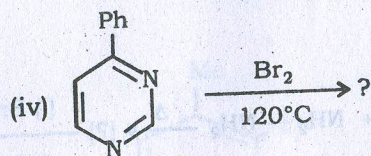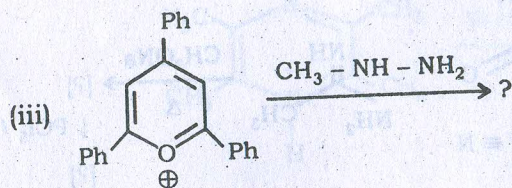(c) Logically develop the synthesis of the following : 3+3

(i)

(ii)

(d) Carry out the following transformation and indicate the product/s in each case with mechanism. 3+2

(i)

(ii)

10. Predict the product with mechanism (any *five*) : 5×3

(i)

$\xrightarrow{\text{MeI}}$?

(ii)

$\xrightarrow[\text{MeOH, r.t.}]{\text{NaOMe}}$?

(iii)

$$\text{(Ph, O}^{\oplus}\text{ pyrylium)} \xrightarrow{CH_3-NH-NH_2} ?$$

(iv)

$$\xrightarrow[120°C]{Br_2} ?$$

(v)

$$\xrightarrow[\text{liq. } NH_3]{NaNH_2} ?$$

(vi)

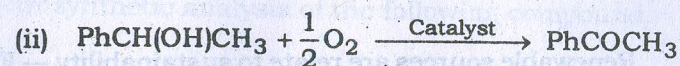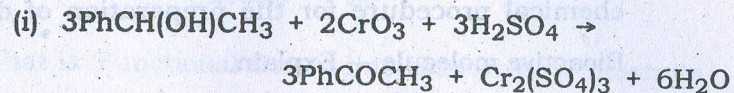$$PhCH_2COCl \xrightarrow[\substack{rt. \\ \text{then } H_2 / Pd}]{CH_2N_2} ?$$

Group—C

(a) What is green chemistry ? 2

(b) Compare the atom efficiencies of stochiometric (i) vs catalytic (ii) oxidation of a secondary alcohol to the corresponding ketone.

(i) $3PhCH(OH)CH_3 + 2CrO_3 + 3H_2SO_4 \rightarrow$

$$3PhCOCH_3 + Cr_2(SO_4)_3 + 6H_2O$$

(ii) $PhCH(OH)CH_3 + \frac{1}{2}O_2 \xrightarrow{Catalyst} PhCOCH_3$

$$+ H_2O$$

(c) Give suitable example of different types of reactions in aqueous solvent (any *two*) : 2

(i) Diels-Alder reaction

(ii) Passerini reaction

(iii) Knovenagel reaction.

(d) How would you synthesize following compounds :

(any *one*)   2

   (i) Citral from isobutene (By BASF Procsss)

   (ii) Biodiesel from Plant oil.

(e) Biocatalytic procedure is more superior than classical chemical procedure for the preparation of different Bioactive molecule — Explain.   2

Or

Renewable sources are relate to sustainability — **Explain.**

(f) Why Ionic liquid is used as green solvent ?   2

(g) Give some examples of unconventional energy sources.   2

(h) Give applications of cyclodextrins. How do cyclodextrins act a regio-selective reagent ?   2+3

(i) Design a suitable receptor for mono potassium salts of dicarboxylic acid, synthesize it and show the mode of its complexation.   1+2+2

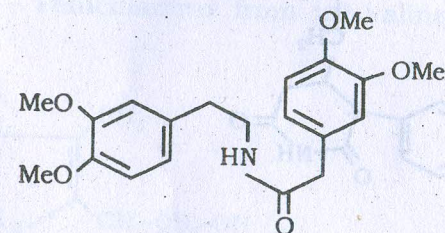*(Organic Special)*

Old Syllabus

F.M. – 75   Time : 3 Hrs.

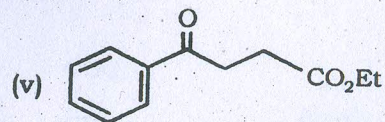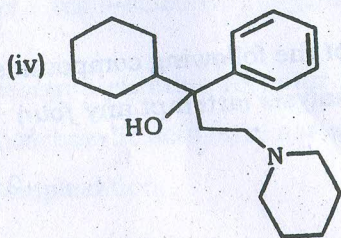Answer any *five* questions taking at least *two* from each group (A and B).
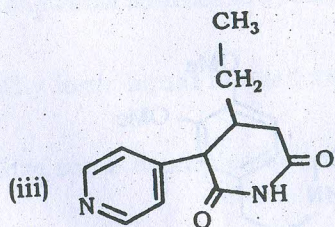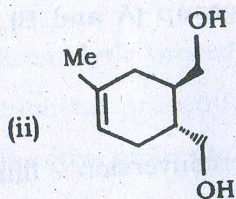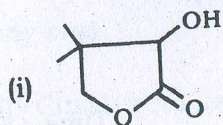
Group — A

1. (a) What is 'Functional Group Interconversion'? Illustrate the use of Functional Group Interconversion in the retrosynthetic analysis of the following compound.


   2+3

(b) Describe the synthesis of the following compounds with proper retrosynthetic analysis (attempt any *four*) :
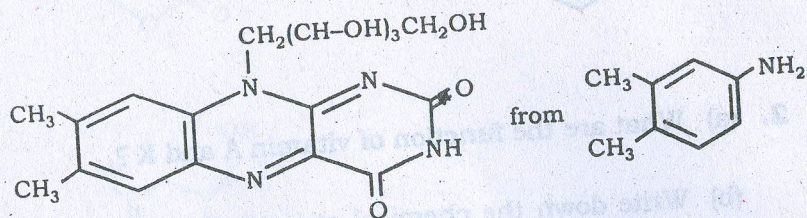
$2\frac{1}{2} \times 4$

(i)

(ii)

(iii)

(iv)

(Continued)

(v)

2. **(a)** What are the function of vitamin A and K ? 2

(b) Write down the chemical structure of Vitamin B_1 and Vitamin C. 2

(c) Write all the steps for the synthesis of the following compounds : 3+4+4

(i) (+) – Penicillamine from (±) valine

(ii)

(Turn Over)

(iii)

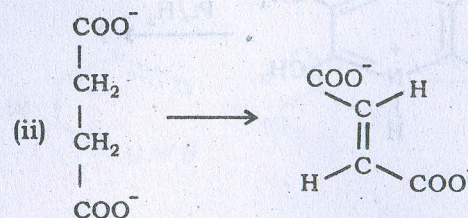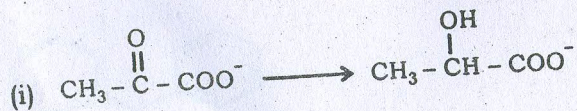$CH_2(CH-OH)_3CH_2OH$ ... from ...
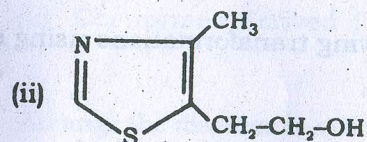
3. (a) Show how conzyme of Vit. B_1 takes part in decarboxylation of pyruvic acid, the end product of carbohydrate metabolism and depict the chemical reactions involved therein.   4

   (b) Carry out the following transformations using enzymes / coenzymes : $1\frac{1}{2} \times 2$

   (i) $CH_3 - \overset{O}{\underset{\|}{C}} - COO^- \longrightarrow CH_3 - \overset{OH}{\underset{|}{CH}} - COO^-$

(ii) $\begin{array}{c} COO^- \\ | \\ CH_2 \\ | \\ CH_2 \\ | \\ COO^- \end{array} \longrightarrow$
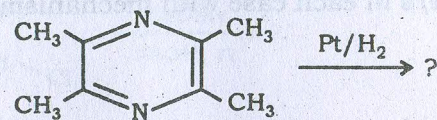
(c) Discuss the mode of action of the following coenzymes derived from various vitamins (with mechanism) :   4+4
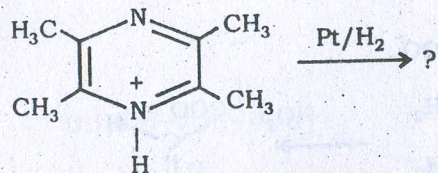
   (i) Coenzyme derived from Thiamine.

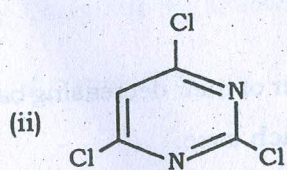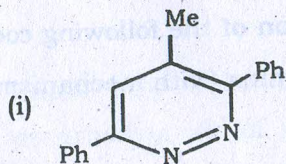   (ii) Coenzymes derived from Riboflavin.

4. (a) Arrange the diazines in order of their decreasing basicities and give explanation for each case.   2

   (b) What would be the product/s when treated as follows and indicate the reason with explanation :   2
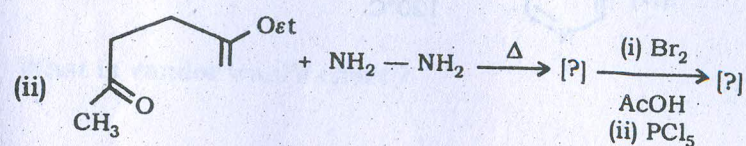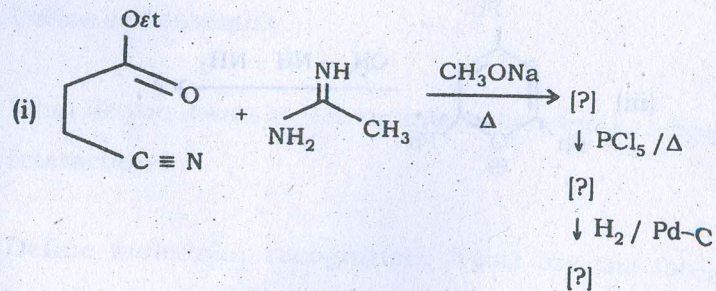

$\xrightarrow{Pt/H_2}$?

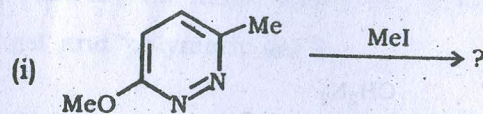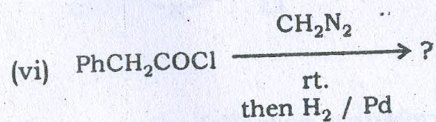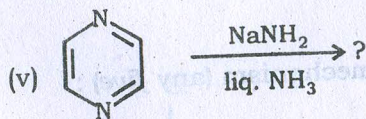(c) Logically develop the synthesis of the following :
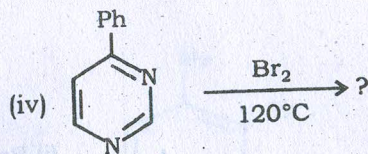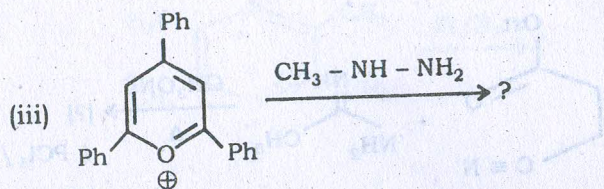
(i)

(ii)

3+3

(d) Carry out the following transformation and indicate the product/s in each case with mechanism. 3+2

(i)

(ii)

5. Predict the product with mechanism (any *five*) : 5×3

(i)

(ii)

(iii)

$$CH_3 - NH - NH_2 \longrightarrow ?$$

Ph, Ph, Ph, O⊕ (structure)

(iv)

$$\xrightarrow[120°C]{Br_2} ?$$

(v)

$$\xrightarrow[\text{liq. } NH_3]{NaNH_2} ?$$

(vi) $PhCH_2COCl$

$$\xrightarrow[\substack{\text{rt.} \\ \text{then } H_2 / Pd}]{CH_2N_2} ?$$
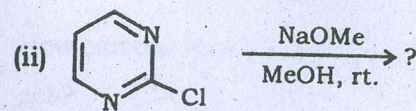
Group — B

6. (a) Define self-assembly. 2

(b) What do you mean by ion-ion interaction and ion-dipole interaction ? 2

(c) Define molecular recognition. What are the forces involved in molecular recognition process ? Design a receptor for adipic acid and illustrate the observation of complexation. 2+2+2+3

(d) What is vander waal's effect ? 2

7. (a) What is a 'supramolecular gel' and how is it formed ? 3

(b) What are the major difference between 'supramolecular gel' and 'polymeric gel' ? 2

(c) Give some examples of Law Molecular Mass Organogelators. 3

(d) How can one study of the morphology of a supramolecular gel ? 3

(e) What is self-replication ?   2

(f) Write briefly the significance of such studies.   2

8. (a) What are cyclodextrins ? What are the major driving forces for cyclodextrin complexation ? Write some applications of cyclodestrins. What is the effect of added α-CD on the following chlorination reaction ? 2+3+3+3
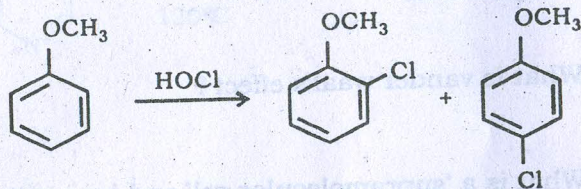
(b) What is molecular mechanic calculation ? Calculate the heat of formation of the following compound.

S.E = 6.3 K.Cal/mole   2+2

9. (a) What is enzymes ? How Hydrogen bonding interaction of base pair in DNA ?   2+3

(b) Illustrate the following secondary structural element of a peptide : α-helix, β-pleated sheet.   3+3

(c) Write the sequence of the mRNA molecule synthesized from and DNA template strand having the sequence :

$$5' - ATCGTACCGTTA - 3'$$ 4

10. (a) Benzyl penicillin (A) $C_9H_{11}N_2O_4SR$, R = benzyl group on treating dilute NaOH yields $C_9H_{13}N_2O_5SR$, (B) which on heating eliminates CO_2 and gives $C_8H_{13}N_2O_3SR$ (C). Compound (C) on hydrolysis with aqueous $HgCl_2$ breaks down to compound $C_3H_4NO_2R$ (D) and $C_5H_{11}NO_2S$ (E). Compound [D] was identified as penilloaldehyde and E as penicillamine. Draw backwards to identify [C], [B], [A] and establish the structure of penicillin through spectroscopic evidences.   4+6

(b) What do you mean by Catabolism and anabolism ? Show the four stages of catabolism. 2+3