2017

M.Sc. Part–II Examination

CHEMISTRY

PAPER—VI

Full Marks : 75

Time : 3 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 *five* questions from group C.

(Turn Over)

Group—A

1. (a) Obtain the expression for the molar rotational entropy of a homonuclear dietomic molecule. 8

   (b) Calculate the molecular translational partition function for hydrogen molecules in a container of volume $100\ cm^3$ at 27°c.
   (Given $k = 1.38 \times 10^{-23}\ JK^{-1}$ and $h = 6.626 \times 10^{-34}\ JS$). 7

2. Define the grand canonical partition function Z, obtain the expression for in Z for particles describable by antisymmetric wave function and hence derive the appropriate distribution law. 2+4+9

3. (a) Establish the prigogine principle of minimum entropy production. 9

   (b) What is meant by phenomenological coefficients ? Write the thermoshynamic equations relating fluxes and forces and state the onsagar reciprocity relations. 2+2+2

4. Derive the expression for the rate of entropy production for a flow in a system when a pressure difference is observed as a result of an electrical potential. Obtain the expression for streaming potential in terms of the phenomenological coefficients. 10+5

Group—B

5. (a) What are Ziegler-Natta catalysts ? 3

   (b) At 25°C, the density of glucose is $1.55\ g\ cm^{-3}$, its diffusion coefficient is $6.81 \times 10^{-6}\ cm^2\ s^{-1}$ and the viscosity coefficient of water is 8.937×10^{-3} poise. Assuming that the glucose molecule is spherical, estimate the molar mass. 5

   (c) For step polymerisation process derive rate equation for both acid catalyzed and non-catalyzed polymarization process. 7

6. (a) Explain the term transmission coefficient for Activated complex theory. 3

   (b) Determine the standard equilibrium constant for a reaction :

   $$N_2(g) \rightleftharpoons 2N(g)\ at\ 5000K$$

   given that : $r_{eq} = 110$ pm for N_2 classical frequency of vibration of $N_2(g) = 7.07 \times 10^{13}\ s^{-1}$ dissociation energy of $N_2(g) = 940.3\ KJ\ /\ mol$.

   The degeneracy of ground electronic level of $N_2 = 1$ and that of $N(g) = 4$. 5

   (c) Give statistical calculation of transition state theory. 7

7. (a) For ionic reaction using single sphere activated complex model derive the expression of rate constant. 6

(b) Explain the influence of ionic strength on reaction rate. 3

(c) For partial microscopic diffusion controlled reaction prove that

$$K = K_{chem}$$

where the symbols indicate usual meaning. 6

Group—C

8. Answer any *five* questions : 5×5

(a) Obtain the expression for pressure of an ideal gas in terms of ground partition function.

(b) Establish the relationship between molecular translational partition function and molar tranlational portition function.

(c) What is potential energy surface ?

(d) Write short notes no flash photolysis.

(e) What is electrostriction ?

(f) Use, without derivation, appropriate expressions to derive the Saxen's relation.

(g) What is macroscopic kinetics and microscopic kinetics ?

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(Organic 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 *five* questions from group C.

Group — A

2

1. (a) Define template effect.

(b) How does macrocyclization work even though it is an entropically disfavorable process ? 2

(c) Name the compound 1 and propose a synthetic route.

1+2

6
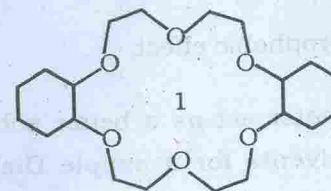
(d) Design a receptor for the complexation of barbiturates. Synthesize the compound. Show complexation with barbiturates. Give evidence for complexation.

2+2+2+2

2. (a) Define cryptands with examples. Why cryptands form stronger complexes than crown ethers ? 2+2

(b) Define the term micelles and reverse micelles. 3

(c) Classify different types of gels. Give some examples of supramolecular gelators. What are the techniques uses for studying the gel morphologies ? What are the major difference between 'supramolecular gel' and 'polymeric gel' ? 2+2+2+2

3. (a) Define co-enzymes and cofactors with examples. 2+2

(b) List three ways in which RNA is different from DNA. 3

(c) Show the H-bond interaction in A-T and G-C base pairs in DNA. 2

(d) Define hydrophobic effect. 3

(e) How can water act as a better solvent than common organic solvents for a simple Diels-Alder reaction ? Illustrate with examples. 3
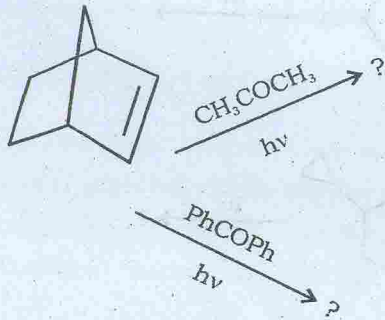
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4. (a) Define Narrish type-I and type-II reactions. Explain each of these reactions with suitable mechanism. 4

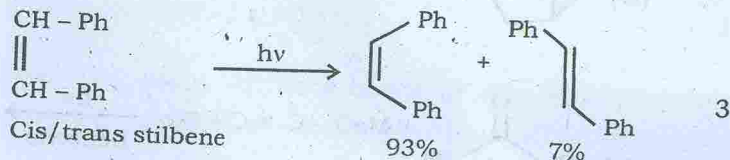(b) Predict the products of the following reaction with mechanism : (attempt any four) 2×4

(i) $\xrightarrow{h\nu}$?

(ii) $\xrightarrow{h\nu}$?

(iii) $\xrightarrow[ROH]{h\nu}$?

(iv) $\xrightarrow{h\nu}$?

(v) Ph $\overset{O}{\underset{}{\|}}$ Ph $+ MeO - C \equiv C - Me \xrightarrow[benzene]{h\nu}$?

(vi) $\xrightarrow[CH_3CN]{h\nu}$?
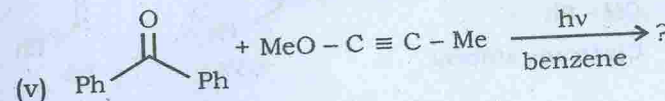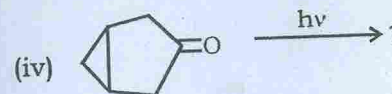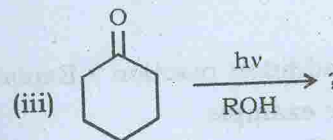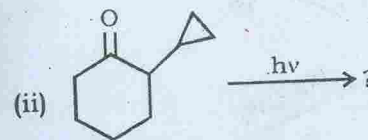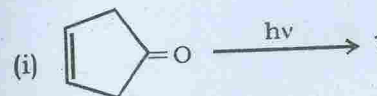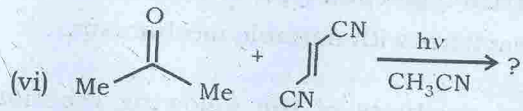
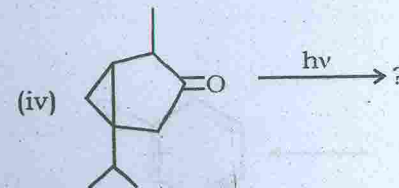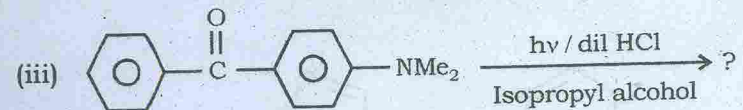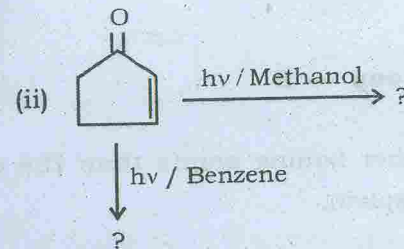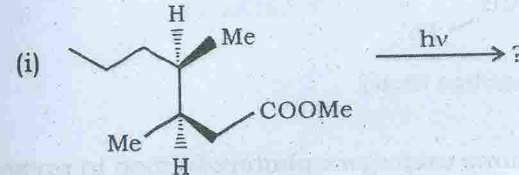(c) Predict the products for the following reaction :

3

5. (a) What is Paterno-Büchi addition reaction ? Explain the mechanism with suitable example. 3

(b) Suggest reasonable explanation for the following observation :

Cis/trans stilbene
93%   7%

3

(c) Predict the products of the following reactions with mechanism : (Attempt any *three*)   2×3

(i) $\xrightarrow{h\nu}$?

(ii) $\xrightarrow{h\nu \, / \, Methanol}$?

$\downarrow h\nu \, / \, Benzene$

?

(iii) $\xrightarrow[\text{Isopropyl alcohol}]{h\nu \, / \, dil \, HCl}$?

(iv) $\xrightarrow{h\nu}$?

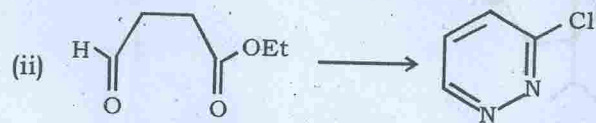(v)

(Crystalline State)
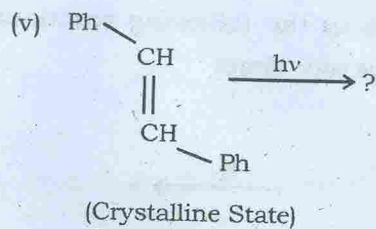
(d) Benzophenone undergoes photoreduction in presence of isopropanol but Michler's ketone does not absorb under the same condition — Explain.   3
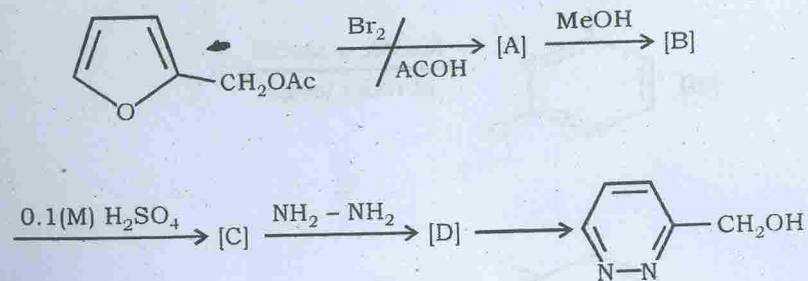
Group — B

6. (a) Pyridazine has higher boiling points than the other diazines — why ? Explain.   2

(b) Carry out the following transformation :
   (Attempt any *three*)   3×3

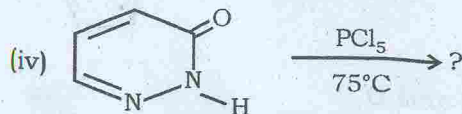(i)

(ii)

(iii)
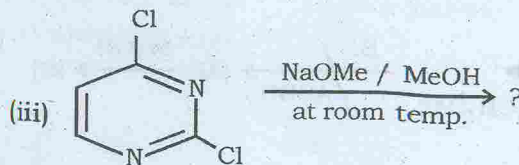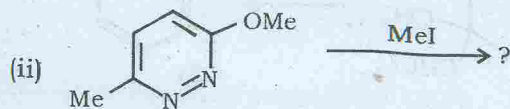

(iv)
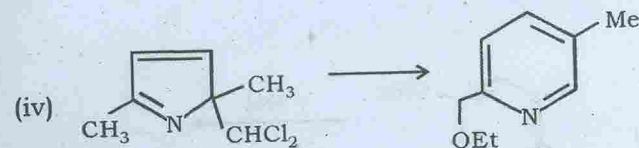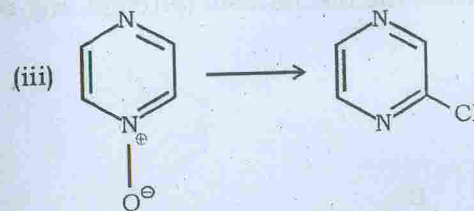
(c) The following is the transformation :

Identify A, B, C and D.   4

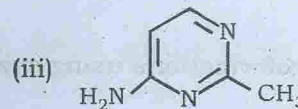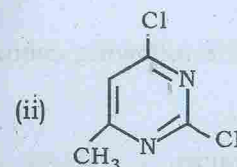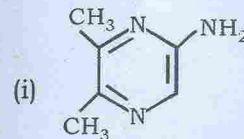**7.** (a) Predict the product(s) in each case of the following reactions. Indicate the mechanism (attempt any *three*) :

2×3

(i)

$\xrightarrow[120°C]{Br_2}$?

(ii)

$\xrightarrow{MeI}$?

(iii)

$\xrightarrow[\text{at room temp.}]{NaOMe \ / \ MeOH}$?

(iv)

$\xrightarrow[75°C]{PCl_5}$?

(Continued)
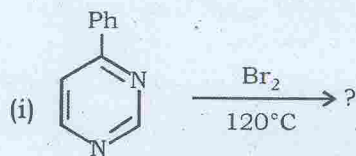
(b) Logically develop the synthesis of the following compounds : (attempt any *three*) .

3×3

(i)

(ii)

(iii)

(iv)

(Turn Over)

(v)
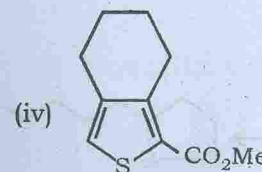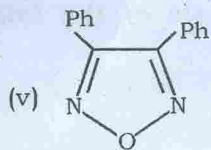
8. (a) What are vitamins ? $\qquad$ 1

(b) What are the functions of vitamin B_1 and C. $\qquad$ $1\frac{1}{2}$

(c) Discuss the mode of action of the following coenzymes derived from vitamins (with ( ))
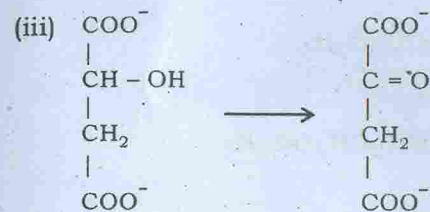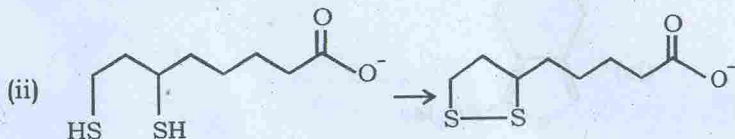
(i) coenzyme derived from Niacin,

(ii) coenzyme derived from pantothenic acid.

$4+4$

(d) Carry out the following transformations using enzymes / coenzymes : (any *two*) $\qquad$ $1+1$

(i) Pyruvate $\longrightarrow$ acetyl–CoA

(ii)

(iii)

(e) Show how TPP acts in the metabolism of carbohydrate. Indicate all the steps involved. $\qquad$ $2\frac{1}{2}$

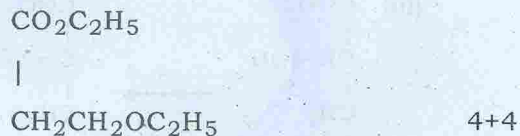**9.** (a) Write down the chemical structure of cephalosporin C and streptomycin and also mention their medical uses.

$2+2$

(b) Write all the steps for the synthesis of the following compounds :

(i) Penicillin V from
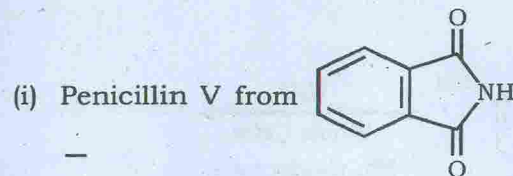
(ii) Thiamine chloride hydrochloride from

$$CO_2C_2H_5$$
$$|$$
$$CH_2CH_2OC_2H_5$$ 4+4
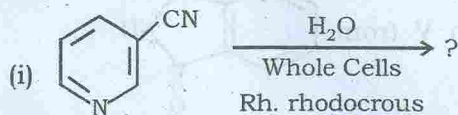
10. (a) What is sustainable development ? 1

(b) How do you synthesize the following compounds :

(i) Caprolactum from cyclohexanone (By sumitomo process)

(ii) Adipic acid from Glucose (Green process). 2+2

(c) Hoechest route is a green route for the prepration of ibuprofen (analgesic) — explain. 2

(d) Predict the product of the following reactions :

(i)

(ii) $Ph-CH_2-$ $\xrightarrow[\text{H-USY}]{\text{MeOH}}$? 1+1

(e) Give examples (Green Synthesis) :

(Attempt any *three*) 3

(i) Aspirin synthesis (Under solvent free)

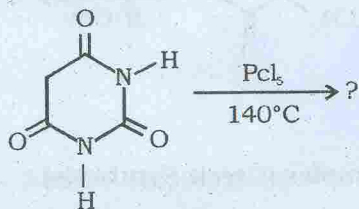(ii) Ring opening metathesis (Under aqueous condition)

(iii) Passerini reaction (Under aqueous condition)

(iv) Iodolactonization (Under aqueous condition)

3

Or

10. (a) "Diazines are weaker bases than pyridine." Explain the statement. 2

(b) Predict the product of the following reaction. Indicate the mechanism.

$\xrightarrow[140°C]{PCl_5}$?   3

(c) Which one is more susceptable between 2-chlor pyrimidine and 4-Chloro Pyrimidine towards nucleophilic substitution ? Explain.   3

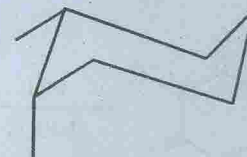(d) Predict the product of the following reaction. Indicate the mechanism.

$\xrightarrow[\substack{(ii) \ TSOH \ / \ Et_2O \\ R.T.}]{(i) \ hv}$?   2
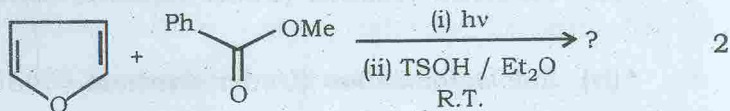
Group—C

(a) What is antibiotics ?   2

Or

What are the different types of penicillin ?

(b) Define gels. Classify the different types of gels.   2+2

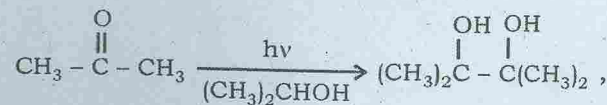(c) Calculate heat of formation of the following compound :

SE = 10.1 K.Cal/mole   2

Or

Write the use of different types of gels.

(d) How can you prepare 6-APA from penicillin a using green technique.   2

(e) Green chemistry related to sustainability — explain.   2

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

(g) What is mean by quantum yield ? The quantum for the reaction

$$CH_3 - \overset{O}{\underset{\|}{C}} - CH_3 \xrightarrow[(CH_3)_2CHOH]{hv} (CH_3)_2\overset{OH}{\underset{|}{C}} - \overset{OH}{\underset{|}{C}}(CH_3)_2 \ ,$$

$$\varphi = 1$$

Explain and suggest a mechanism for the reaction, which is consistant with the above data.   5

(h) Predict the product of the following reaction. Indicate the mechanism.

$\xrightarrow[140°C]{PCl_5}$? 3