West Bengal State University

B.A./B.Sc./B.Com. (Honours, Major, General) Examinations, 2015

PART-III

CHEMISTRY– Honours

Paper– VI

(New and Old Syllabus)

Duration : 4 Hours

Full Marks : 100

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

The figures in the margin indicate full marks.

(New Syllabus)

Use separate answer scripts for [**CEMAT-36-OA & CEMAT-36-OB**]

and for [**CEMAT-36-PA & CEMAT-36-PB**]
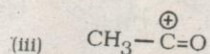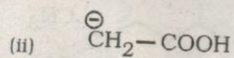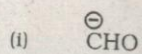
CEMAT-36-OA

Answer any *two* (2) questions taking *one* (1) from each Unit.

UNIT - I

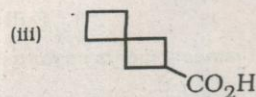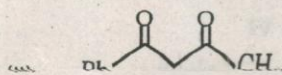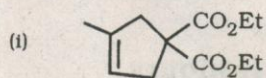1. a)   Write down the synthetic equivalents of the following synthons (any *two*) :

$2 \times 1 = 2$

  (i) $\overset{\ominus}{C}HO$

  (ii) $\overset{\ominus}{C}H_2 - COOH$

  (iii) $CH_3 - \overset{\oplus}{C} = O$

[Turn over

b)   Describe the synthesis of the following compounds with proper retrosynthetic analysis (any *two*) : $2 \times 2\frac{1}{2} = 5$

(i)

(iii)

c)   Predict the products of the following reactions from FMO consideration (any *two*) : $2 + 2 = 4$

(i)

(ii)

(iii) $(E, E)-CH_3CH=CHOCH_2CH=CHCH_3 \xrightarrow{\Delta} ?$
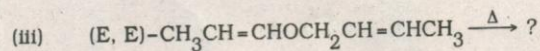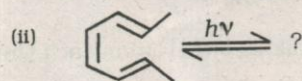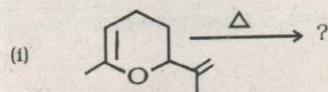
d)   Anthracene acts as a diene — explain with an example.   2

2.   a)   Using protection-deprotection technique, carry out the following transformation :   2

b) Predict the products in the following reactions (any *two*) : 2 × 2 = 4

(i) $\xrightarrow{\Delta}$?

(ii) $\xrightarrow{\Delta}$?

(iii) $\overset{\Delta}{\rightleftharpoons}$?
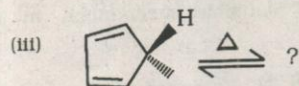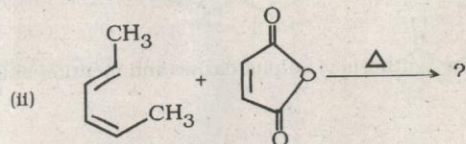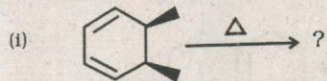
c) Write short notes on the following (any *two*) : $2 \times 2\frac{1}{2} = 5$

(i) Illogical Electrophiles

(ii) Favorskii Rearrangement

(iii) Umpolung .
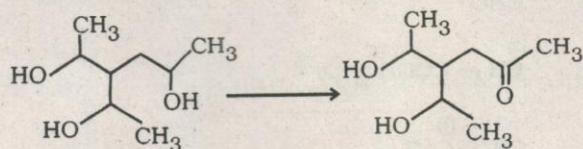
d) Why does Phenanthrene act as an alkene ? Explain with an example. 2

UNIT - II

3. a) Predict the products with plausible mechanism : $2 \times 2\frac{1}{2} = 5$

(i) $\xrightarrow[Et_2O]{PhLi}$?

(ii) $\xrightarrow[DMF]{CH_2Cl_2/CH_3Li}$?

Left margin notes: with proper $2 \times 2\frac{1}{2} = 5$; consideration $2 + 2 = 4$; 2; the following; 2

SUB.-B.Sc.(HN)-CEMA-12044   [Turn over
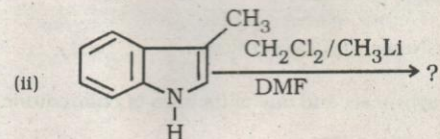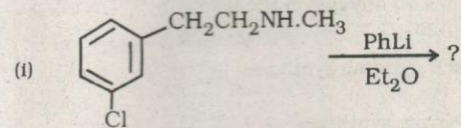
b)   Carryout the following transformation.   3
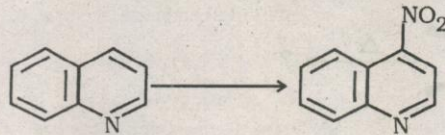
c)   Write down the synthesis of sulphadiazine and mention one of its uses.

                                                         3 + 1

4.   a)   Predict the products with plausible mechanism in the following (any *two*) : $2 \times 2 = 4$

(i)

(ii)

(iii)
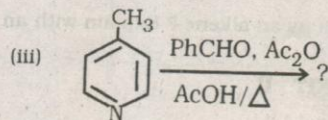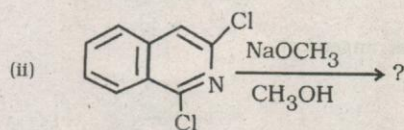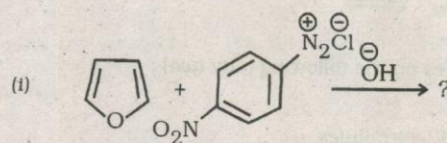
b)   Write short notes on any *two* of the following : $2 \times 2\frac{1}{2} = 5$

(i)   Hantzsch pyridine synthesis

(ii)   Knor Pyrrole synthesis

(iii)   Bischler-Napieralsky sysnthesis.

c)   Write down the synthesis and one of its uses of chloroquine. $2 + 1$

CEMAT - 36-OB

Answer any *two* (2) questions taking *one* (1) from each Unit.

UNIT-I

5.   a)   The rate of chromic acid oxidation of *cis-4-t*-butylcychohexanol at 25°C is about four times faster than that of its *trans*-isomer. Explain rationally.   3

      b)   Explain why (any *two*) : $2 \times 2\frac{1}{2} = 5$

          (i)   Unlike glucose, arabinose shows abnormal mutarotation.

          (ii)   Sucrose is known as a reducing sugar.

          (iii)   Two molecules of $PhNHNH_2$ are required for the formation of one molecule of osazone of glucose.

      c)   What are the symmetry elements present in the boat form of Cyclohexane ?   2

      d)   How can you convert *D*-arabinose to *D*-fructose ?   3

6.   a)   Explain the following with proper reasoning (any *two*) : $2 \times 2\frac{1}{2} = 5$

          (i)   *cis*-4-hydroxycyclohexane carboxylic acid is heated.

          (ii)   4, 4-dimethylcyclohexanone forms cyanohydrin at a slower rate than does cyclohexanone.

          (iii)   For *trans*-2-chlorocyclohexanol, both the diaxial and diequatorial forms are almost equally populated.

      b)   What is mutarotation ? Why does glucose show mutarotation in aqueous solution ? Will glucose exhibit mutarotation in 2-hydroxypyridine ? Explain.   1 + 2 + 1

      c)   Compare the stabilities of chain form, boat form and twist boat form of cyclohexane.   3

      d)   What is a glucoside ?   1

[Turn over

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3

on one of its uses.

3 + 1

in the following

$2 \times 2 = 4$

$2 \times 2\frac{1}{2} = 5$

quine.   2 + 1

UNIT-II

7. a) Show that the following molecule obeys special isoprene rule.   1
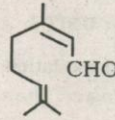
    b) Write the structures of A and B.   2
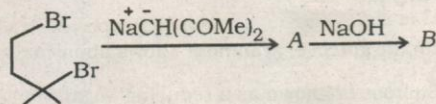
    c) How can you prove that 3-substituted pyridine nucleus is present in nicotine ?   2

    d) Write the structure of alanine in dry solid state. What will be its predominating forms at pH = 0 and pH = 14. $1 + \frac{1}{2} + \frac{1}{2}$

    e) Synthesize phenylalanine using Erlenmeyer azlactone synthesis.   3

    f) During peptide synthesis benzoylation is not used as a protecting group of amine — Why ?   2

8. a) Write the structures of A, B, C, D, E in the following reaction sequence :

                                                       $\frac{1}{2} + 1 + \frac{1}{2} + \frac{1}{2} + \frac{1}{2}$
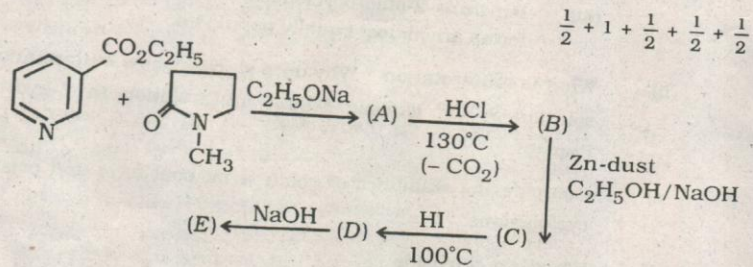
b) Draw the structures of citral-a and citral-b. How can you convert citral into geraniol ? $\qquad$ 1 + 1

prene rule.   1

c) Outline Edman method for the determination of N-terminal amino acid residue of a polypeptide. In what respect this method is superior to Sanger's method ? $\qquad 2\frac{1}{2} + 1\frac{1}{2}$

2

d) A tetrapeptide of unknown sequence was shown to contain Ala, Gly, Phe and Val in equimolar ratios. Further experiment showed —

nucleus is present in
2

(i) valine was the N-terminal amino acid residue.

te. What will be its
$1 + \frac{1}{2} + \frac{1}{2}$

(ii) hydrolysis of the tetrapeptide yielded a number of fragments of which one was tripeptide composed of Gly, Phe and Val. Also present in the hydrolysis mixture was a dipeptide composed of ala and gly. Determine the amino acid sequence of the tetrapeptide.   3

e synthesis.   3

OR

is a protecting group
2

Write down the structure of ninhydrin. How can you detect an α-amino acid using this ? $\qquad$ 1 + 2

reaction sequence :

$\frac{1}{2} + 1 + \frac{1}{2} + \frac{1}{2} + \frac{1}{2}$

CEMAT-36-PA

Answer any *two* (2) questions, taking *one* [1] from each Unit.

UNIT - I

B)

Zn-dust
$C_2H_5OH/NaOH$

9. a) Deduce Boltzmann distribution formula for a non-degenerate system. Assume $\beta = \dfrac{1}{K_B T}$.

b) Define partition function. Express Helmholtz free energy (A) and internal energy (U) of a system in terms of partition function.

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[Turn over

c) Is it possible to attain very low temperature by adiabatic demagnetisation ? Explain. $5 + (1 + 2 + 2) + 3$

10. a) Calculate using Boltzmann distribution the ratio of population at 27°C of energy levels separated by

   (i) 10 KT

   (ii) 1000 cm^{-1}.

   b) Deduce Einstein equation for heat capacity of solid. Show at high temperature it resembles Dulong-Petit's law. State the limitations of Einstein equation and explain how it is modified by Debye.

   c) Calculate the molecular partition function for a system which consists of energy states 0, 2KT and 4KT with the degeneracies 1, 2 and 3 respectively. $(2 + 2) + (4 + 3) + 2$

Unit - II

11. a) What is Raman effect and how does it differ from phosphorescence and fluorescence ?

   b) Why water cannot be used as a solvent in infrared spectroscopy.

   c) State Frank-Condon principle.

   d) ~~What is vibration-rotation spectra ?~~

   e) The rotational spectrum of HF has lines 41·9 cm^{-1} apart. Calculate the moment of inertia and bond length of HF molecule. $3 + 2 + 2 + 1 + 4$

12. a) H_2 molecule does not give IR spectrum but HD molecule does. Explain.

   b) The wave number of vibration of HCl^{35} molecule is 2990 cm^{-1}. Calculate the force constant of HCl bond.

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c) Differentiate between hot bands and overtones in IR spectrum. 'Vibrational spectra are band spectra.' Explain.

d) For HCl, B = 10·59 cm^{-1}, and the fundamental and first overtone vibrational band is shown around 2885 cm^{-1} and 5679 cm^{-1} respectively. Calculate the hot band wave numbers. 2 + 3 + (2 + 2) + 3

CEMAT-36-PB

Answer any *two* (2) questions taking *one* (1) from each Unit.

Unit - I

13. a) State the law of rational indices. Determine the Miller indices of the planes that intersect the crystallographic axes at —
   (i) a, 2b, c
   (ii) a, b, − c.

b) KCl has *fcc* lattice, but from *X*-ray diffraction experiment it appears to be simple cubic. — Explain.

c) Find the spacing of (110) planes in *bcc* crystal with unit cell volume 27 × 10^{-24} cm^3.

d) What is meant by polarizability of a molecule ? How does molar polarisation of polar molecules vary with temperature ?
   (2 + 2) + 3 + 2 + 4

14. a) Adsorption of gas on a solid surface is an exothermic process. Justify.

b) Derive Langmuir adsorption equation. Suggest a suitable linear plot for its verification.

c) The surface tension of dilute solution of a solute varies with the solute concentration C_2 as $\gamma = \gamma_0 - ac_2$, where γ_0 is the surface tension of pure solvent and a is a constant. Show that $\Gamma_2 = \dfrac{\gamma_0 - \gamma}{RT}$.

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[Turn over

d) Define total polarization (P_t). How can the dipole moment be determined with the help of Debye's equation ? $\qquad$ $2 + (3 + 2) + 3 + 3$

UNIT-II

15. a) Derive thermodynamically using chemical potential a relation between the elevation of boiling point of a dilute solution and molal concentration of the solute. State the assumptions involved.

b) Explain the lowering for vapour pressure of a solution of non-volatile non-electrolyte solute with respect to the pure solvent.

c) A 0.1 molal aqueous solution of a weak electrolyte ionising into two ions freezes at $-0.208°C$. Calculate the degree of dissociation $\left[K_f = 1.86\right]$.

d) An azeotrope is not a pure compound. — Explain. $(4 + 2) + 2 + 2 + 2$

16. a) Derive Duhem-Margules equation. Show that if Raoult's law is applicable to one of the constituents of a binary liquid mixture at all composition, it must be equally applicable to the other constituent.

b) Draw the phase diagram of phenol-water system and explain the various lines.

c) What is critical solution temperature ? Cite an example of a binary liquid system that have two critical solution temperatures. $(4 + 2) + 3 + (2 + 1)$

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