लक्ष्यं विश्रमानम्

WEST BENGAL STATE UNIVERSITY

B.Sc. Honours PART-III Examinations, 2017

CHEMISTRY-HONOURS

PAPER-CEMA-VI

Time Allotted: 4 Hours | Full Marks: 100

The figures in the margin indicate full marks. Candidates should answer in their own words and adhere to the word limit as practicable. Use separate answer scripts for Organic and Physical sections. All symbols are of usual significance.

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

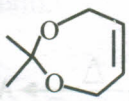
CEMAT-36-OA

Answer any *two* questions taking *one* from each unit

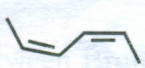
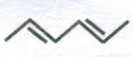
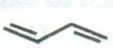
Unit-I

1. (a) What is high dilution principle in the synthesis of large ring compounds? 1.5

   (b) Synthesise the following compounds showing the retrosynthetic pathway (any *two*) 2.5×2 = 5

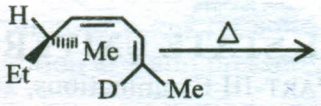
   (i)  (ii)  (iii) $Me_3CCH(CO_2Et)$

   (c) Arrange the following dienes in decreasing rate of Diels-Alder reaction with maleic anhydride. Give reason. 2.5

   (i)  (ii)  (iii)  (iv) 

   (v) 

(d) Predict the product with stereochemistry of the following reaction. Designate the pericyclic step involved therein. 2



(e) Write Bogert-Cook synthesis of phenanthrene. What is the utility of using 2-methylcyclohexanone in place of cyclohexanone in this synthesis? 2

2. (a) Give synthetic equivalents for the following : 1.5

(i) $\overset{\ominus}{C}O_2H$ (ii) $\overset{\oplus}{C}H_2 - CH_2OH$ (iii) $CH_3 - \overset{\oplus}{C} = O$

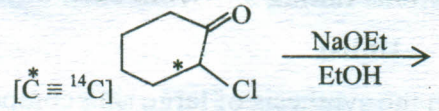
(b) Use protecting group to transform (any *one*) : 2.5

(i) 

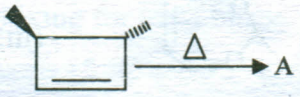
(ii) $CH_3{-}\overset{O}{\overset{\|}{C}}{-}CH_2CH_2CH_2CO_2Et \longrightarrow CH_3{-}\overset{O}{\overset{\|}{C}}{-}CH_2CH_2CH_2CH_2OH$

(c) Convert naphthalene to 2-aminonaphtalene. 2

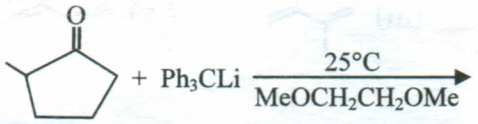
(d) Predict the product(s) with plausible mechanism: 3



(e) Predict the structure of 'A' and explain the following reaction from FMO theory. 1+2



(f) Predict the major enolate with proper explanation in the following where base is added to excess ketone. 1

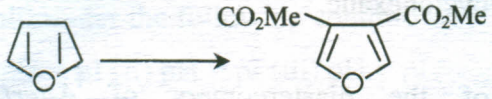


Unit-II

3. (a) Carry out the following transformation (any *two*) 2×2

(i) Pyridine ⟶ 4-nitropyridine

(ii) Aniline ⟶ 4-methylquinoline

(iii) 

(b) Explain the following observation: 2

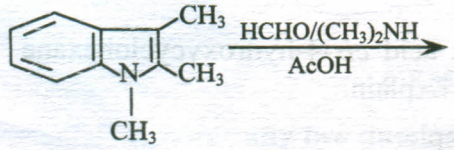
Electrophilic attack takes place at C_2 in Pyrrole but at C_3 in Indole.

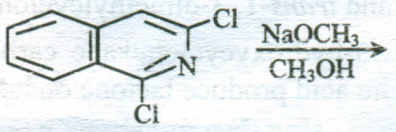
(c) Outline the synthesis and therapeutic use of Ranitidine. 3+1

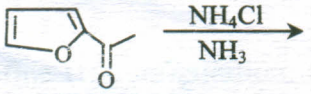
(d) What happens when quinoline is treated with Br_2 in CCl_4? 2

4. (a) Write down a synthesis of Sulphadiazine and mention one important use of the compound. 3+1

(b) Predict the product(s) in the following reactions and suggest mechanism in each case. (any *two*) 2.5×2 = 5

(i) 

(ii) 

(iii) 

(c) Nucleophilic Substitution at 2-chloroquinoline takes place at a faster rate than that at 2-chloropyridine. Explain. 3

CEMAT-36-OB

Answer any *two* questions taking *one* from each unit

Unit-I

5. (a) Between Bromine-water and ammoniacal $AgNO_3$, which one do you prefer for oxidation of D-glucose into D-gluconic acid? Justify your choice. 2.5

(b) How will you convert D-fructose into D-glucose? 2.5

(c) Write down the preferred conformers of the following with explanation. 3

(i) 1-methyl-1-phenylcyclohexane.

(ii) *trans*-1, 3-ditertiarybutylcyclohexane.

(d) Acetolysis of optically active *trans*-2-acetoxycyclohexyl tosylate gives a racemic mixture of *trans*-1, 2-diacetoxycyclohexane. 2

Explain the observation with reason.

(e) Relative rates of saponification of the diastereomers of 4-*tert* butylcyclohexyl *p*-nitrobenzoates (**X**) and ethyl 4-*tert*-butyleyclohexane carboxylates (**Y**) are as follows: 3

for '**X**' $K_{trans}/K_{cis} = 2.5$ whereas for 'Y' $K_{trans}/K_{cis} = 20$. Give an explanation.

6. (a) What is reducing sugar? Explain with an example. 2

(b) Explain why glucose and fructose form the same osazone. 3

(c) Compare the stabilities in terms of gauche-butane interaction of the following pairs: 3

(i) *cis*- and *trans*-1, 2-dimethylcyclohexane

(ii) *cis*- and *trans*-1, 3-dimethylcyclohexane

(d) Both *cis*-3-hydroxycyclohexane carboxylic acid *cis*-4-hydroxycyclohexane carboxylic acid produce lactone on heating. Explain. 3

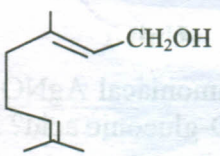
(e) What is mutarotation? Explain with an example. 2

Unit-II

7. (a) Write down a scheme for the synthesis of Gly-Ala using DCC prompted peptide bond formation. Give mechanism for the DCC coupling reaction. 3

(b) Synthesise $RCH_2CH(NH_2)\ CO_2H$ from RCHO. 2

(c) What is special isoprene rule? Show whether the following compound obeys the said rule: 3



(d) How could you establish that nicotine possesses 3-substituted pyridine nucleus? 2

(e) How will you convert? 2

$$PhCOEt \longrightarrow (\pm)\text{-ephedrine}$$

8. (a) In an electric field, towards which electrode would an amino acid migrate (if at all) under the following conditions? 3

(i) pH < pI (ii) pH > pI (iii) pH = pI

Explain your answer.

(b) How can you establish that the stereocentre in (–)-nicotine has S-configuration? 2.5

(c) How could you establish that a tripeptide consisting of three different α-aminoacids has alanine as its C-terminal residue? 2.5

(d) Write the products formed in the following reaction : 2

$$\text{Citral} \xrightarrow[\text{(ii) } CrO_3]{\text{(i) } KMnO_4} ?$$

(e) Write down the product(s) when ethyl ester of (±)- alanine is heated? 2

CEMAT-36-PA

Answer any *two* questions taking *one* from each unit

Unit-1

9. (a) Define (i) configuration, and (ii) thermodynamic probability. Entropy is a logarithmic function of thermodynamic probability– Justify. 2+2

(b) Three identical but distinguishable particles are distributed among three energy levels 0, E and $2E$. Write down the different possible distributions of the particles for total energy (i) E and (ii) $2E$. Also obtain the thermodynamic probability for each distribution and hence the change in entropy for increasing the total energy from E to $2E$. 1+2+2

(c) The total number of microstates (W_T) of a system of 'N' distinguishable particles, distributed in two energy states is given as $W_T = 2^N$. Using Stirling's approximation, find the number of microstates ($W_{1:1}$) for the distribution with (N/2) particles in each energy state. Compare W_T and $W_{1:1}$ and comment. 4

10.(a) State and explain the third law of thermodynamics. Draw a curve showing the variation of entropy when a solid (at temperature T) is slowly heated to form vapor at temperature T_1 (T_1 > boiling point) at constant pressure. 4

(b) For two nondegenerate energy levels, separated by an amount of energy $\Delta\varepsilon = 500\,k_B$, at what temperature will the population in the higher-energy state be half of that of the lower energy state? Give calculation. 3
[k_B = Boltzmann Constant]

(c) The third law of thermodynamics leads to that: $\left(\frac{\partial V}{\partial T}\right)_p$ approaches zero as temperature, T approaches zero. Justify/criticise. 2

(d) Derive the barometric distribution formula using Boltzmann distribution law. 4

Unit-II

11.(a) Which of the following molecule absorb in the microwave region of electromagnetic radiation: HCl and N_2. Give reason? 2

(b) Show that the rotational spectral line spacing is constant and is equal to 2B, where B is the rotational constant of the molecule. 3+2

The rotational spectrum of HF has lines 41.9 cm^{-1} apart. Calculate the moment of inertia of the molecule.

(c) What is the difference between overtones and hot bands in connection to IR spectroscopy? 2

(d) The equilibrium vibration frequency of the iodine molecule is 215 cm^{-1} and the anharmonicity constant, is 0.003. At 300 K what is the intensity of the 'hot band' relative to that of the fundamental line? 3

12.(a) Discuss the effect of isotopic substitution on the rotational spectrum with the example of $^{12}C^{16}O$ and $^{13}C^{16}O$. 3

(b) Which of the following molecules are IR-active? Give reasons. 2
H_2, CO_2, HCl.

(c) A heteronuclear diatomic molecule of reduced mass 1.63×10^{-24} g absorbs at 2880 cm^{-1} of light. Calculate the force constant of the molecule assuming harmonic oscillator model. 3

(d) What is meant by Raman effect? How does it differ from Rayleigh scattering? Mention two important characteristics of Raman spectra. 2+2

CEMAT-36-PB

Answer any *two* questions taking *one* from each unit

Unit-I

13.(a) Show that the distance of separation between two successive *hk*-planes in a two dimensional square is $\frac{a}{\sqrt{h^2+k^2}}$, where '*a*' is the unit distance along X and Y axes. 3+1

Comment on the possibility that the distance between two successive parallel planes in a cubic crystal is $\frac{a}{\sqrt{7}}$.

(b) Calculate the fraction of space occupied by particles in a close-packed face-centred cubic lattice. 2

(c) Potassium crystallises with a body-centered cubic lattice and has a density of 0.856 g cm^{-3}. Calculate the length of the unit cell and the distance between (110) planes. 3

(d) What is the highest order that can be observed in Bragg's reflection from a crystal of inter-planner distance 2Å by X-ray, having wavelength 100 pm? 2

(e) The dielectric constant of a liquid at 25°C is 4.288. The molar mass of the liquid is 1.12 g mol^{-1} and its density at that temperature is 1.188 g cm^{-3}. Calculate the value of its molar polarization. 2

14.(a) Arrange, with explanation, the following molecules in order of increasing dipole moment. CH_3Cl, CH_2Cl_2, $CHCl_3$ 3

(b) Surfactants form micelles in water - Why? 2

(c) Estimate the fraction of void space in the face centred cubic lattice. 2

(d) Distinguish between Smectic and Nematic liquid crystals with reference to their behaviour to X-ray and magnetic field. Give one example for each type. 3

(e) In the Langmuir model of absorption of a gas on solid if rate constant of adsorption is equal to that of desorption at 1 atm pressure, the surface is 50% covered. Justify / criticise. 3

Unit-II

15.(a) Define colligative property, 'Colligative properties are intensive in nature'. Comment. 2

(b) From the chemical potential versus temperature diagram justify that $\Delta T_f > \Delta T_b$. Assume that the solute is non-volatile and does not dissolve in solid solvent. 3

(c) The total vapour pressure at 25°C of a mixture of benzene and toluene, in which the two mole fractions are equal is 62 mm Hg. The vapour pressure of pure benzene at 25°C is 95 mm Hg. Calculate the mole fraction of benzene in the vapour in equilibrium with the liquid mixture, (assume ideal behavior of the mixture). 3

(d) "Four phases of sulphur cannot co-exist at equilibrium"-Justify. 2

(e) Calculate the degree of freedom for an azeotrope in two-component liquid-vapour equilibria. 2

16.(a) Derive thermodynamically the Van't Hoff equation of osmotic pressure of solution. Mention any assumptions and approximations made. 5

(b) Calculate the osmotic pressure of 5% solution of cane sugar at 25°C. 2

(c) Show that the change in volume of mixing for ideal binary solution is zero. 2

(d) The vapour pressure of a liquid between 15 °C and 35 °C fits the expression: $\log(p/\text{torr}) = 8.750 - 1625/(T/K)$. Calculate (i) the enthalpy of vaporisation and (ii) the normal boiling point of the liquid. [Given, 1 atm = 760 torr] 3