WEST BENGAL STATE UNIVERSITY

B.Sc. Honours Part-III Examination, 2022

CHEMISTRY

PAPER: CEMA-VI

Time Allotted: 4 Hours | Full Marks: 100

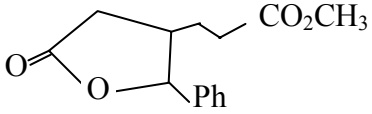
The figures in the margin indicate full marks.
Candidates should answer in their own words and adhere to the word limit as practicable.
All symbols are of usual significance.

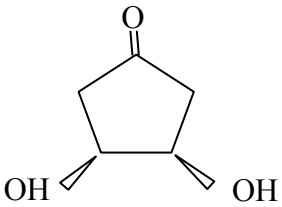
CEMAT-36-OA

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

UNIT-I

1. (a) Analyse the following compounds retrosynthetically and outline a plausible synthetic route leading to them (any ***one***): 3

(i) 

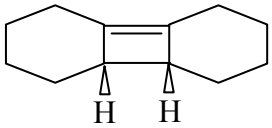
(ii) 

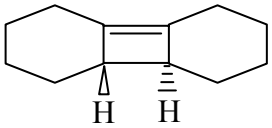
(b) Explain the term 'synthetic equivalent' and 'functional group addition' giving example in each case. 2

(c) Write down the mechanism of the following reaction showing proper stereochemical approach towards the preferred diastereomer. 2

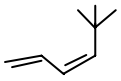
$$(R)-PhCH(Et)CHO \xrightarrow[THF]{MeMgBr} ?$$

(d) Which of the following compounds will undergo thermal electrocyclic ring opening at a faster rate? — Explain. 2





(e) Which one of the following two compounds acts as a better diene in Diels-Alder reaction and why? 2

(i) 

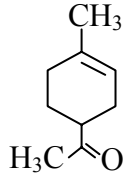
(ii) 

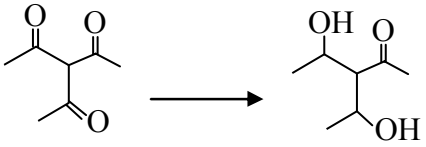
(f) Carry out the following transformation with a plausible mechanism. 2

β-Naphthol $\longrightarrow$ β-Naphthylamine

2. (a) Phenanthrene reacts with diazomethane but anthracene doesn't. — Explain. 2

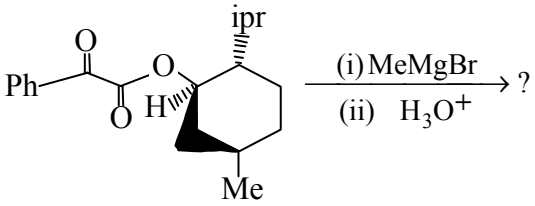
(b) How can you prepare the following compounds as directed? (any ***one***): 2

(i) 

(ii) 

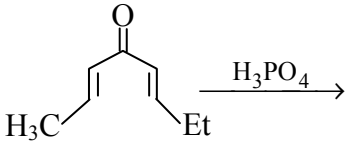
(using Diels Alder reaction) (using proper protection and deprotection)

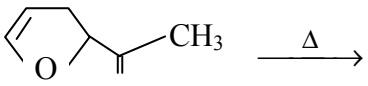
(c) Predict the major diastereomer in the following reaction. 2+1 = 3



What is the basis of your prediction?

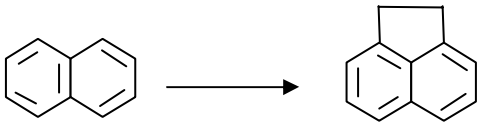
(d) Rationalise the fates of the following reactions in terms of FMO interactions. (any ***one***): 2

(i) 

(ii) 

(e) The two isomeric compounds $PhCH_2–COCH_2Br$ and $PhCH(Br)COCH_3$, on heating with aq. $^{(-)}OH$, give the same product. Identify the product with plausible mechanism. 2

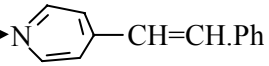
(f) How do you carry out the following conversion? 2

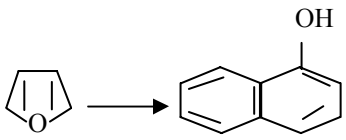


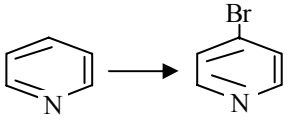
Unit-II

3. (a) How would you synthesize 2-chloro-4-methylquinolene and 4-chloro-2-methylquinoline separately from the same starting material? Explain with mechanism. 2+2

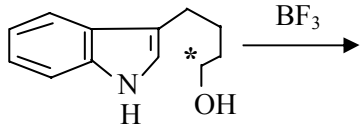
(b) Carry out the following transformations (any ***two***): 2+2

(i) 4-methylpyridine 

(ii) 

(iii) 

(c) Complete the reaction and explain with mechanism. 2

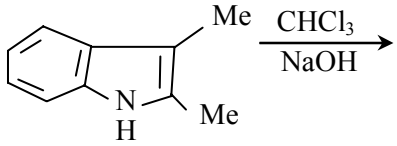


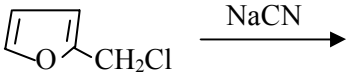
(d) Arrange the following species in order of decreasing delocalization energies. Justify your choice. 2

Pyrrole , Furan , Thiophene , Benzene

4. (a) Write down the synthesis of Sulphadiazine and mention one important use of this compound. 2+1

(b) Predict with proper justification the product(s) in the following reactions. 3

(i) 

(ii) 

(c) What happens when quinoline and pyridine are treated with Na in liq ammonia separately? Explain with suitable mechanism. 3

(d) Describe Fischer indole synthesis of 2-methylindole. Write plausible mechanism. How would you demonstrate which nitrogen is lost during cyclisation? 2+1

CEMAT-36-OB

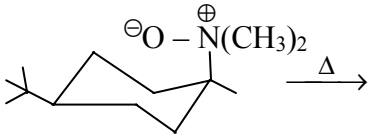
Answer any *two* questions taking *one* from each unit

UNIT-I

5. (a) Draw a structure of *trans*-1,3-dimethylcyclohexane in chair form, then write its flip form. Find out the relationship between the two structures. $\frac{1}{2}+\frac{1}{2}+1=2$

(b) Draw an energy diagram for the chair to chair interconversion of cyclohexane mentaining a plane of symmetry during interconversion. 2

(c) Predict the major products in the following reactions with mechanism. $1\frac{1}{2}+1\frac{1}{2}=3$

(i) 

(ii) D-Glucose $\xrightarrow[\Delta]{\text{Conc. HCl}}$

(d) Draw the preferred conformation, with reason, of *trans*-1,3-di-*tert*-butylcyclohexane. On heating with Pd/C it readily passes to its *cis*-isomer. — Explain. 2

(e) Explain the following observations: 2+2 = 4

(i) Tollens' oxidation of D-fructose gives a mixture of the salts of D-gluconic acid and D-mannonic acid.

(ii) In aqueous medium D-glucose exists mainly in β-anomeric form whereas D-mannose exists chiefly in α-anomeric form.

6. (a) Arrange the following dichlorocyclohexanes in order of decreasing amount of (a, a) form present in their conformational equilibrium. Give reasons. 3

trans-1, 4-dichlorocyclohexane, *cis*-1,3-dichlorocyclohexane,

trans-1, 2-dichlorocyclohexane

(b) Explain the formation of the products when D-glucose is separately allowed to react with acetone/dry HCl and benzaldehyde/dry HCl. 3

(c) β-D-glucose is oxidized to gluconolactone with bromine-water at a much faster rate than α-D-glucose. — Explain. 2

(d) Which diastereomer of 4-*tert*-butylcyclohexanol undergoes faster chromic acid oxidation and why? 2

(e) How would you justify the fact that all the methyl pyranosides of α-D-hexose series have the same configuration at C–1 and C–5? 3

Unit-II

7. (a) Draw the stereoisomers of citral. Device a chemical method for the determination of the configuration of the stereoisomers of citral. 3

(b) Most amino acids form a purple product when heated with ninhydrin. Draw the mechanism for the formation of a coloured product when valine is treated with ninhydrin. 3

(c) Synthesise the tripeptide gly.phe.ala by solid phase peptide synthesis methodology. Explain the choice of protecting groups in this synthesis. 3

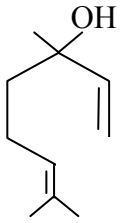
(d) How will you prepare phenylalanine by Erlenmeyer Azlactone synthesis? 2

(e) Give the CIP configurational descriptor of L-cysteine. 1

8. (a) What happens when ephedrine is boiled with aq. HCl? Explain the formation of the product(s). 2

(b) Complete the following reactions showing mechanism: 3+2 = 5

(i) $RCHO + CH_2(CN)CO_2Et \xrightarrow[Pd-C\,/\,H_2]{NH_4OAc\,/\,AcOH} M \xrightarrow[(ii)\ HNO_2]{(i)\ N_2H_4} N \xrightarrow[(ii)\ HCl]{(i)\ EtOH} O$

(ii) 

$\xrightarrow{H^+\,/\,H_2O} P \xrightarrow{dil\ H_2SO_4} Q$ (slow formation)

(c) Write down the most populated structures of aspartic acid [$HO_2CCH_2CH(NH_2)COOH$] and lysine [$H_2N(CH_2)_4CH(NH_2)COOH$] at their isoelectric points. Explain your answer. 2

(d) What is the difference between isoelectric point and isoionic point? 1

(e) Using 2,5-diketopiperizine how would you synthesize dl-tyrosine? 2

CEMAT-36-PA

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

UNIT-I

9. (a) For an ensemble consisting of N particles and having only two non-degenerate energy levels at 0 and $h\nu$, if the average energy of an ensemble unit, $\langle \varepsilon \rangle = -\frac{1}{q}\left(\frac{dq}{d\beta}\right)$, then find the total energy of the ensemble in terms of ν. 3

[Given: q = molecular partition function, $\beta = 1/kT$]

(b) Do you expect the residual molar entropies for crystalline 1,2-difluorobenzene and 1,4-difluorobenzene to be the same? Give explanation. 3

(c) If the average energy, U of an ensemble consisting of N particles is, $U = Nh\nu/(e^{\beta h\nu} + 1)$, find the expression of heat capacity in terms of β. [Given: $\beta = 1/kT$] 3

(d) Consider a system of eight distinguishable particles to be distributed among seven energy levels having energies of 0, 1, 2, 3, 4, 5 and 6 Joule. If the total energy is 4 Joule, find the most probable distribution of the particles among the energy levels such that $\sum n_i = 8$ and $\sum n_i \varepsilon_i = 4$ Joule and hence find the thermodynamic probability of such distribution. [Assume that each level can be occupied by any number of particles, n_i = number of particles in i-th level, ε_i = energy of the i-th level.] 2+2

10.(a) Evaluate the partition function for a collection of equispaced non-degenerate levels. 3

(b) Is absolute zero obtainable by adiabatic demagnetisation? Explain describing the principle of adiabatic demagnetisation using a schematic S-T diagram. 1+3

(c) Barometric distribution is a special case of the more general distribution, Boltzmann distribution law. Justify or criticise. 3

(d) State Nernst heat theorem. What do you mean by residual entropy? $1\frac{1}{2}+1\frac{1}{2}$

Unit-II

11.(a) State and explain which of the following molecules will be infrared active. 3

HCl, HD, O_2, N_2O

(b) State the essential requirement for a molecule to be microwave active. Obtain an expression for the line spacing in the microwave spectra of a diatomic rigid rotor. 2+3

(c) The rotational constant B of $^{*}C^{16}O$ molecule is 55.35×10^{9} s^{-1} and the equilibrium bond length is 1.128×10^{-10} m. Find the isotopic mass of $^{*}C$ atom. 4

12.(a) In pure rotational Raman spectrum of a diatomic molecule the separation of the first line from the exciting line is $6B$ cm^{-1}, while that between successive lines is $4B$ cm^{-1}. — Explain. [Given: B = rotational constant] 3

(b) For a diatomic molecule, behaving as anharmonic oscillator, the maximum vibrational quantum number, v_{max} , is given by, $v_{max} = \frac{1}{2\tilde{x}_e} - 1$. 3

($\tilde{x}_e$ is anharmonicity constant).

(c) The spectrum of HCl shows very intense absorption at 2886 cm^{-1}, a weaker one at 5668 cm^{-1}, and a very weak one at 8347 cm^{-1}. Calculate the fundamental frequency, ω_e and the anharmonicity constant, x_e. 3

(d) Explain the Stokes and anti-Stokes lines in Raman spectra according to the classical theory of Raman effect. 3

CEMAT-36-PB

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

UNIT-I

13.(a) Although NaCl and KCl have same crystalline structures reflection from (111) planes is present in NaCl crystal but that is missing in KCl crystal. — Explain. 3

(b) The dipole moment of ortho-xylene is 0.693 Debye. Find the dipole moment of toluene and para-xylene. 3

(c) Considering identical atoms in a cubic crystal as hard spheres of equal size, in packing of the spheres if the edge of the unit cell is $2/\sqrt{3}$ times the diameter of the sphere, find the percent of void space in the crystal. 3

(d) The molar polarization of the vapour of a compound was found to vary linearly with $1/T$ and is 75.74 cm^3mol^{-1} at 320.0 K. If the dipole moment of the molecule is 0.968 D, calculate the polarizability volume of the molecule. 4

[Given: ε_0 (vacuum permittivity) = 8.854×10^{-12} $J^{-1}C^2m^{-1}$, 1D = 3.33564×10^{-30} Cm]

14.(a) Define polarizability, α and molar polarization, p of a substance. Under what condition on α, p is constant? State how dielectric constant and density of the substance are interrelated under this condition. 4

(b) Write down the BET equation of adsorption explaining the terms involved and hence state the principle of determination of the surface area of a finely divided solid. 4

(c) Explain the following equation along with the terms involved. 2

$$d = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

(d) A substance known to have a cubic unit cell gives reflections with radiation of wavelength 137 pm at the glancing angles 10.7° and 17.7°. If the reflection at 17.7° is known to be due to the (111) planes, index the other reflection. 3

Unit-II

15.(a) Derive thermodynamically using chemical potentials a relation between the depression of freezing point of a solvent and the molal concentration of nonvolatile solute dissolved in it pointing out the assumptions and approximations involved if any. 4+2

(b) Liquid carbon dioxide cannot exist at normal atmospheric pressure whatever be the temperature. — Justify. 2

(c) The normal boiling temperature of benzene is 353.24 K, and the vapour pressure of liquid benzene is 1.19×10^4 Pa at 20.0°C. If the triple point temperature is 278 K then find the triple point pressure. 4

16.(a) Explain Eutectic point, Eutectic temperature and Eutectic composition with the help of a phase diagram. 3

(b) What is an azeotropic mixture? How would you ascertain that an azeotrope is a mixture, not a compound? 3

(c) The molecular origin of Raoult's law is the effect of solute on the entropy of the solution. Explain qualitatively. 2

(d) A mixture of 100 g water and 80 g of phenol separates into two layers at 60°C. One layer, L_1, consists of 44.9% water by mass; the other L_2, consists of 83.2% water by mass. Calculate the total number of moles in L_1 and L_2. 4

[Given: molar mass of phenol = 94.11 g mol^{-1}]

N.B. : *Students have to complete submission of their Answer Scripts through E-mail / Whatsapp to their own respective colleges on the same day / date of examination within* 1 *hour after end of exam. University / College authorities will not be held responsible for wrong submission (at in proper address). Students are strongly advised not to submit multiple copies of the same answer script.*

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