# WEST BENGAL STATE UNIVERSITY

B.Sc. Honours Part-III Examination, 2020

## CHEMISTRY

## PAPER-CEMA-VI

Time Allotted: 2 Hours Full Marks: 50

*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.*

### CEMAT-36-OA

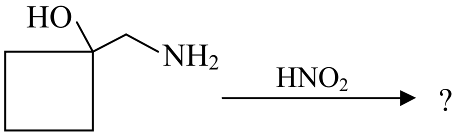
**Answer any *one* question from either UNIT-I OR UNIT-II**

### UNIT-I

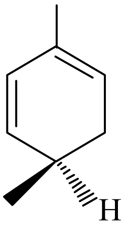
1. (a) How can you synthesise 4-oxopentanoic acid ($MeCOCH_2CH_2COOH$) using an illogical nucleophile? 2

(b) Predict the major diastereomeric product when *S*-3-chloro-2-butanone is treated with sodium borohydride. 2

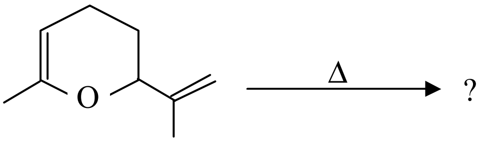
(c) Predict the product of the following reaction with suitable mechanism: 2



(d) The following compound undergoes easy racemisation when heated. — Explain. 2



(e) Complete the following transformation: 2+1

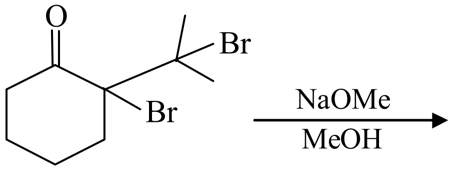


Suggest a suitable mechanism for the thermal rearrangement of the above compound. Also comment on the geometry of the transition state involved in the above reaction.

(f) How could you synthesize anthracene starting from naphthalene using Diels Alder reaction as one of the key step? 1

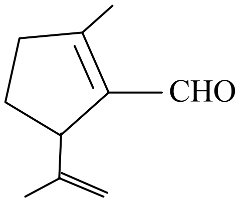
2. (a) How can you convert glycerol into $HOCH_2COCH_2OH$? $1\frac{1}{2}$

(b) Predict the product of the following reaction and suggest mechanism for its formation. $1\frac{1}{2}$

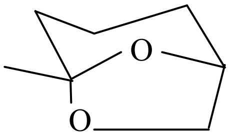


(c) Give retrosynthetic analysis and efficient synthesis of any ***one*** of the following compounds. 2

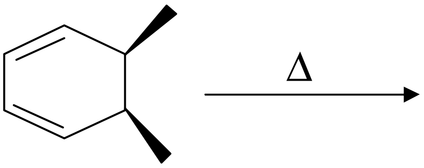
(i)



(ii)



(d) Predict the product of the following reaction and show the FMO interactions. 2



(e) Thermal dimerisation of cyclopentadiene gives preponderantly the *endo* cycloadduct under kinetically controlled conditions. — Explain. 2

(f) Phenanthrene was oxidized by $CrO_3$ in acetic acid. The product was warmed with aqueous ethanolic KOH followed by acidification. The resulting compound then heated in air to yield a carbonyl compound. Identify the sequence of steps. 3

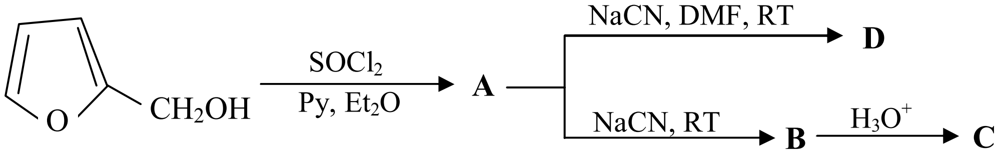
## Unit-II

3. (a) Account for the following observations showing the products in each cases.

(i) Furan and pyrrole react differently with maleic anhydride. 2

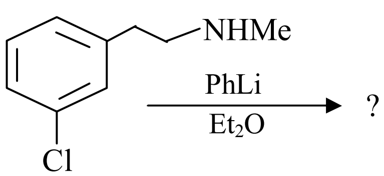
(ii) Indole undergoes nitration in the heterocyclic nucleus but nitration of quinoline occurs in the carbocyclic ring. 2

(b) Give the products of the following reactions with necessary explanations: 3

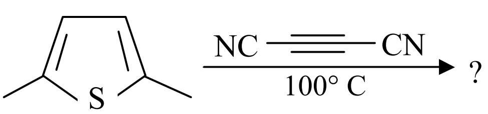


(c) Give products for the following reaction: $1\frac{1}{2}\times2=3$

(i)

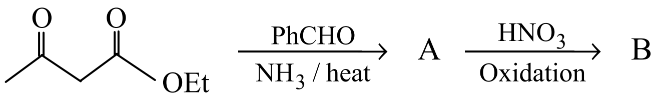


(ii)



(d) Outline the synthesis of metronidazole. 2

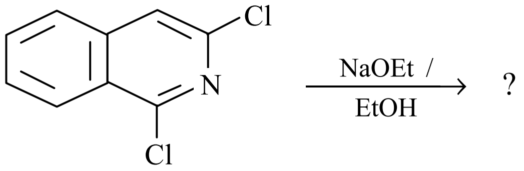
4. (a) Identify A and B in the following reaction sequence with the suitable mechanism. 3



(b) How would you transform *o*-nitrotoluene to indole? 2

(c) Indole 2-acetic acid undergoes easy decarboxylation in boiling water. — Explain. 2

(d) Give the product of the following reaction. Suggest a plausible mechanism. 2



(e) Write down the synthesis of ranitidine and mention one important use of the compound. 2+1

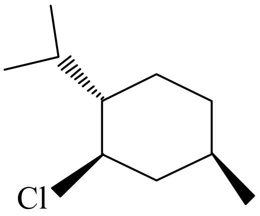
## CEMAT-36-OB

### Answer any *one* question from either UNIT-I OR UNIT-II

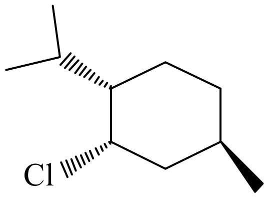
### UNIT-I

5. (a) Both the diastereomers of 2-acetoxycyclohexyl tosylate when acetolysed in presence of AcOH/$AcO^-$ gave the *trans*-1,2-diacetoxycyclohexane as the sole product, but *trans*-isomer reacts 660 times faster than that of *cis*-isomer. — Explain. 3

(b) Explain which one of the following compounds will react at faster rate under base catalysed dehydrochlorination condition. 2



and



(c) What are the symmetry elements present in the boat and twist boat forms of cyclohexane? Comment on their optical activity. 2

(d) Explain the following observations: 2+2

(i) *D*-glucose exhibits mutarotation in the presence of 2-hydroxypyridine but not in the presence of pyridine itself.

(ii) *β*-*D*-glucose is more stable than *α*-*D*-glucose but methyl *β*-*D*-glucoside is less stable than methyl *α*-*D*-glucoside.

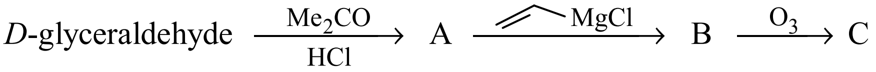
(e) How can you convert *D*-glucose into a 3-O-methyl-D-glucose? 2

6. (a) *Cis* 1,2-dimethylcyclohexane is optically inactive though it possesses no $S_n$ axis. 2

(b) Both *cis*-1,2-dibromocyclohexane and *cis*-1-bromo-2-chlorocychexane are chiral but only one of them displays optical activity at room temperature. — Explain. 3

(c) Write down the most stable conformations of (i) *trans*-1,3-di-*tert*-butyl cyclohexane, (ii) 1-phenyl-6-*tert*-butylcyclohexene. 2

(d) Complete the following reaction sequences and identify the products (A, B and C). 3



(e) Dilute $HNO_3$ oxidation of *D*-glucose and another aldohexose give the same aldonic acid. Write down the structure of this aldohexose with proper reasoning. 3

## Unit-II

7. (a) How can you synthesise phe-ala-gly using Merrifield protocol? 3

(b) L-Alanine reacts with nitrous acid to produce mainly L-lactic acid. Show with a reasonable mechanism. 2

(c) Define isoelectronic point. The *pKa* values of glutamic acid are 2.19, 4.25 and 9.67. Calculate the isoelectronic point of glutamic acid. 3

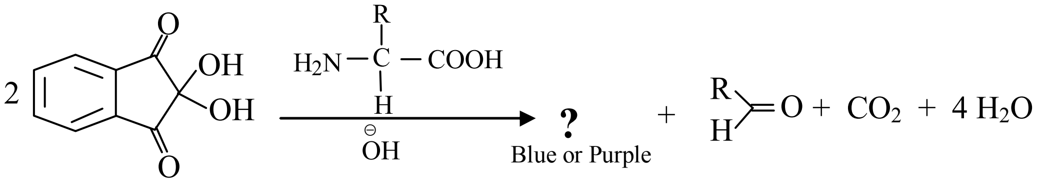
(d) What happens when citral is heated with anhydrous potassium hydrogen sulfate? What information about the structure of citral is obtained from the reaction? How can you show that the structure of citral obeys special isoprene rule? 3

(e) How can you show that nicotine contains a pyridine and a pyrrolidine ring system? 2

8. (a) Among 2,4-dinitrofluorobenzene and phenylisothiocyanate which one is more useful for determination of the N-terminal amino-acid sequence of a polypeptide chain and why? Explain with proper illustration. 3

(b) Write down the structure of L-(-)-hygrinic acid. How this compound helps us to confirm the stereochemistry of naturally occurring nicotine? 3

(c) Predict the following product with mechanism. 3



(d) Explain the following observations: 2+2

(i) Acid catalysed cyclisation to *α*-terpineol occurs 9 times faster for nerol than for geraniol.

(ii) Ephedrine reacts with diphenyl borinic acid at a much slower rate than pseudo ephedrine.

## CEMAT-36-PA

### Answer any *one* question from either UNIT-I OR UNIT-II

### UNIT-I

9. (a) Which state function of the system is related to maximum value of thermodynamic probability and how? 3

(b) With the help of Maxwell Boltzmann distribution show that the molecular partition function is the ratio of the total number of molecules to the number of molecules in the ground level. 3

[Assume that energy of the ground level, $\epsilon_0$, is zero and this level is non-degenerate.]

(c) For a system of $N$ molecules and with internal energy, $U$ using Maxwell-Boltzmann distribution show that 4

$$U = NkT^2\left[\frac{d\ln f}{dT}\right] \quad [f = \text{molecular partition function}]$$

(d) A system of $N$ particles (distinguishable), has, among others two energy levels with $g_1 = 2$, $g_2 = 3$, $U_1$(energy) = 41.84 $\text{kJmol}^{-1}$ and $U_2$ (energy) = 58.58 $\text{kJmol}^{-1}$. Calculate the ratio of the number of particles in the two energy levels at 1000 K. 3

10.(a) What is meant by Einstein temperature? To which property is it related? Give the equation. 3

(b) The number of molecules in three consecutive energy levels are 1000, 100 and 10 respectively. Show that the distribution is according to Boltzmann statistics. 3

(c) What do you mean by 'residual entropy'? Calculate the molar residual entropy of a crystal in which the molecules can adopt 6 orientations of equal energy at 0 K. 3

(d) According to the Debye theory, the low-temperature molar heat capacity of nonmetallic solids is 4

$$\overline{C}_P(T) = 1943(T/\theta_D)^3\,\text{JK}^{-1}\text{mol}^{-1} \ \text{ for } \ 0 < T \le T_{\text{low}}$$

where $T_{\text{low}}$ is about 10 K to 20 K and $\theta_D$ = Debye characteristic temperature. Using third low show that the low-temperature contribution to the molar entropy is given by

$$\overline{S}(T) = \frac{\overline{C}_P(T)}{3} \ \text{ for } \ 0 < T \le T_{\text{low}}$$

## Unit-II

11.(a) Show that the relative population, including degeneracy, of the rotational energy levels of a rigid diatomic molecule is maximum at the nearest integral $J$ value to 4

$$J_{\max} = \sqrt{\frac{kT}{2hcB}} - \frac{1}{2} \quad \text{(Terms have their usual meaning)}$$

(b) Comment on the Raman activity of the symmetric stretching mode of the fundamental vibrations of carbon dioxide molecule. Give explanation. 3

(c) In the IR spectrum of rigid diatomic molecule a single line is observed at the oscillation frequency of the molecule. — Explain. 3

(d) The rotational spectrum of $^{79}\text{Br}\,^{19}\text{F}$ shows a series of equidistant lines 0.71433 $\text{cm}^{-1}$ apart. Calculate the bond length of the molecule. 3

[Given: atomic masses in kg: $^{79}\text{Br} = 131.03\times10^{-27}$, $^{19}\text{F} = 31.55\times10^{-27}$]

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

[Rotational constant = B]

(b) Show the change in the schematic plot of the relative populations of degenerate rotational energy levels of a diatomic molecule versus rotational quantum number when the rotational constant becomes larger. 3

(c) For the ideal harmonic oscillator the spectral absorption occurs exactly at the classical vibration frequency but for real anharmonic molecules the observed fundamental absorption frequency deviates from the equilibrium frequency considerably. — Justify. 3

[Consider diatomic molecule]

(d) The fundamental and first overtone transitions of NO molecule are centred at 1876 $cm^{-1}$ and 3724 $cm^{-1}$ respectively. Evaluate (i) the equilibrium vibrational frequency and (ii) the zero-point energy. 2+2

## CEMAT-36-PB

### Answer any *one* question from either UNIT-I OR UNIT-II

### UNIT-I

13.(a) What is the lowest limit of the spacing of the lattice planes to produce X-ray diffraction spectra for a given radiation? 2

(b) An element occurs in two crystalline forms $\alpha$ and $\beta$. The $\alpha$-form has FCC structure with $a$ = 3.68 Å and $\beta$-form has BCC structure with $a$ = 2.92 Å. Calculate the ratio of their densities. 3

(c) The molar polarization of fluorobenzene vapour is 70.62 $cm^3 mole^{-1}$ at 351 K and 62.47 $cm^3 mol^{-1}$ at 423 K. Calculate the dipole moment of the molecule. 3

(d) State the law of rational indices. Determine the Miller indices of the planes that intersect the crystallographic axes at (i) $a, 2b, c$ (ii) $a, b, -c$. 2+2

14.(a) State the main steps of surface reaction according to Langmuir-Hinshelwood mechanism. For unimolecular surface reaction find the condition under which the adsorption follows Langmuir adsorption isotherm. 1+3

(b) Mention two important types of liquid crystals. Give one example for each type. Give the vapour pressure-temperature diagram for the substance forming liquid crystal. 2

(c) Copper crystal has density of 8.930 g $cm^{-3}$ at 20°C. If the atoms touch along face-diagonal of the cubic unit cell, find the crystallographic radius of the copper atom. 3

[Given molar mass of Cu = 63.55 g $mol^{-1}$]

(d) At 0°C, the relative permittivity of liquid chlorine trifluoride is 4.75 and its density is 1.89 g $cm^{-3}$. Find the molar polarization of the liquid. 3

[Given: molar mass of chlorine trifluoride is 92.45 g $mol^{-1}$]

## Unit-II

15.(a) Derive Duhem-Margules equation and from it, write the Konowaloff's Rule. 4+2

(b) "It is possible for a solvent in a solution to have elevation of freezing point." — Explain. 2

(c) The normal boiling point of a binary solution of $A$ and $B$ with mole fraction of $A$, $x_A = 0.6589$ is 88°C. At this temperature, the vapour pressure of pure liquids $A$ and $B$ are 957 and 379.5 torr respectively. Is the binary solution ideal? Give reasons in favour of your answer. 4

16.(a) Derive thermodynamically the relation between the elevation of boiling point of a dilute solution containing non-volatile solute and the molal concentration of the solution. State the assumptions involved. 4+1

(b) What is the principle of isobaric fractional distillation? 3

(c) "An Azeotrope is not a pure compound" — Explain. 2

(d) "Colligative properties are intensive in nature" — Justify or criticize. 2

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