



WEST BENGAL STATE UNIVERSITY

B.Sc. Honours 2nd Semester Examination, 2020

CEMACOR04T-CHEMISTRY (CC4)

Time Allotted: 2 Hours

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.

Answer any three questions taking one from each unit

<u>Unit-I</u>

- 1. (a) Account for the following observations.
 - (i) The following compound undergoes racemisation faster for X= H, Y=Br than for X=Br, Y=H.



- (ii) Intramolecular H-bonding is stronger in (2S, 3S)-2,3-butanediol than in the (2R, 3S)-2,3-butanediol.
- (b) Identify the topic relationships (homotopic, enantiotopic or diastereotopic) between 3 the ligands marked 'a' and 'b' in the following compounds.



- (c) Draw Newman projection of all the conformers of n-butane and designate 3 appropriate Klyne-Prelog terminology to each conformer.
- (d) Assign appropriate configurational descriptors $(R_a \text{ or } S_a)$ to the following 2 molecules.



(e) Draw P-gauche conformation of 2,3-dimethylbutane.

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Full Marks: 40

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2. (a) Which of the following compounds will be optically active? Explain.



(b) Label the marked hydrogen atom (\mathbf{H}^*) as *pro-R*, *pro-S*, *pro-E* or *pro-Z* (any *two*)



- (c) Write down +*sc* and -*ac* conformations of 2-methylbutane for rotation around C2-C3. Can you represent these conformations in Fischer Projection? Explain your answer.
- (d) *meso* CH₃CHClCHClCH₃ is achiral despite having chiral conformers Justify.
- (e) Draw the *s*-*cis* and *s*-*trans* conformations of furan-2-aldehyde [A]. Comment on their populations in polar solvents and also in gaseous state. Can you differentiate these by dipole moment values?



Unit-II

3. (a) In the following reaction sequence C has a lower free energy than A, and $k_2 \gg k_{.1} \gg k_1$. Draw the energy profile diagram for the given reaction sequence. How many transition states are involved in this case? To which of the above three species (A, B, C), the transition states will be closest chemically?

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

- (b) Arrange the following compounds in the increasing order of acidity and explain.
 4-Nitrophenol; 2,6-dimethyl-4-nitrophenol; 3,5-dimethyl-4-nitrophenol;
 2,4-dinitrophenol.
- (c) Which one of the following pair of compounds has higher enol content? Explain.



(ii) CH₃CH₂COCH₃ and CF₃CH₂COCH₃

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- (d) What is secondary kinetic isotope effect? Explain with a suitable examples.
- (e) The following reaction (I) occurs at a faster rate than the reaction (II). Suggest explanation.



- (f) Give an example of ring-chain tautomerism.
- 4. (a) Explain the following observations.
 - (i) PhCOCH₂COCF₃ enolises slower than PhCOCH₂COCH₃ although the former is more acidic than the latter.
 - (ii) Enol content of 2,4-pentanedione is 92% in *n*-hexane and 15% in water.
 - (b) How does a catalyst speed up a reaction? Explain with the help of energy profile 2 diagram.
 - (c) Write the structure of corresponding conjugate acid or base in the following cases.



(ii)
$$\left(\begin{array}{c} N \\ N \\ H \end{array} \right) \xrightarrow{H^+} ?$$

(d) Arrange the following compounds with increasing order of basicity in aqueous 3 medium and explain

$$CH_3NH_2$$
, $(CH_3)_2NH$, $(CH_3)_3N$

(e) Which of the following two species is stronger base and which one is stronger 2 nucleophile? Give reasons.

$$\mathrm{HS}^{igodot}$$
 and HO^{igodot}

(f) Give an example of valence tautomerism.

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Unit-III

5. (a) Identify the products formed as **A** and **B** in the following reactions. Suggest 4 plausible mechanism for their formation.

$$\mathbf{B} \stackrel{\text{I. Ag}_2\text{O}, \text{Dil. NaOH}}{\text{II. H}^+} \quad H_3\text{C} \stackrel{\text{Br}}{\longrightarrow} OH \stackrel{\text{I. Conc. NaOH}}{\xrightarrow{\text{II. H}^+}} \mathbf{A}$$

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(b) Which of the following two pathways for the bromination of toluene is more favourable? Explain.



- (c) Me₃CBr undergoes both S_N1 and E2 elimination at a faster rate than $(CD_3)_3CBr$. Is the same type of kinetic isotope effect involved in both the cases? Explain.
- (d) Suggest appropriate reagents for the following transformations.



(e) Select suitable solvent(s) for S_N1 and S_N2 type reactions in general from the 2 following list.

- 6. (a) Explain the following observations:
 - (i) The *erythro*-isomer of 1-bromo-1,2-diphenylpropane undergoes base-induced dehydrobromination at a much slower rate than the *threo*-isomer does.
 - (ii) Towards S_N2 reaction, the susceptibility of alkyl halides follows the order: $EtBr > {}^{i}PrBr > {}^{t}BuBr$, while towards E2 reaction, the order is exactly the opposite.
 - (b) What is the advantage of using a phase transfer catalyst in a substitution reaction? Explain your answer.
 - (c) Account for the stereochemical course involved in each step of the following reaction sequence and give three-dimensional structures (with *R* or *S* designations) for the compounds A to E.

R-1-Deuterioethanol
$$\xrightarrow{\text{SOCl}_2}$$
 A $\xrightarrow{\text{CH}_3\text{COOK}}_{\text{acetone}}$ B $\xrightarrow{\text{KOH/H}_2\text{O}}_{\text{heat}}$ C
 $E \xleftarrow{\text{Nal}}_{\text{acetone}}$ D

(d) Predict the product formed in the following reaction.



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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Memorial Co

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