

WEST BENGAL STATE UNIVERSITY

B.Sc. Honours 4th Semester Examination, 2020

CEMACOR10T-CHEMISTRY (CC10)

Time Allotted: 2 Hours Full Marks: 40

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 four questions taking one from each unit

Unit-I

- 1. (a) Nitriles undergo both acidic and alkaline hydrolysis but isonitriles are hydrolysed only by acids. Explain with mechanism.
 - (b) Give the product with plausible mechanism explanation of the following reaction.

(c) Carry out the following conversions.

$$NH_2$$
 HO NH_2

- 2. (a) Compare the reactions of aniline, N-methyl aniline and N,N-dimethylaniline towards benzenesulfonyl chloride and aq. KOH. How can you utilize this reaction for the separation of primary, secondary and tertiary amines?
 - (b) How can you chemically distinguish between 4-nitro toluene and PhCH₂NO₂?
 - (c) How can you convert aniline into 1, 2, 3-tribromobenzene?

Unit-II

3. (a) Identify the products in the following and show the plausible mechanism involved.

(i)
$$R = {}^{t}Bu$$
 (ii) $R = {}^{t}Bu$? $R = {}^{t}Bu$ Case II: $R = {}^{t}Bu$

2

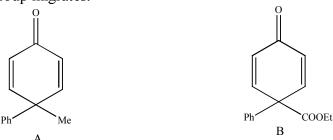
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- (b) Explain the following observations.
 - (i) In the dienone-phenol rearrangement of compound A the phenyl group migrates but in the dienone-phenol rearrangement of compound B the —COOEt group migrates.

2+2

2



- (ii) In the Hofmann degradation of RCONH₂ a small amount of CO(NHR)₂ and RNHCONHCOR are produced along with R-NH₂.
- 4. (a) Predict the products in the following reactions and formulate plausible mechanism for their formation. (any *two*).

i.
$$\begin{array}{c} OH \\ i. \ H_2O_2/NaOH \\ ii. \ dil. \ H_2SO_4 \end{array}$$
 ii.
$$\begin{array}{c} OH \\ ii. \ OH \\ \hline ii. \ H/H_2O \end{array}$$
 iii.
$$\begin{array}{c} OH \\ \hline ii. \ H/H_2O \end{array}$$

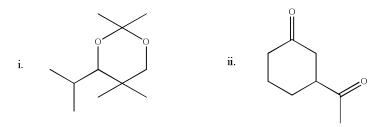
(b) Predict the product (with proper stereochemistry) in the following reaction with suitable mechanistic explanation.

Me
$$C_2H_5$$
 Xylene, H_2O , heat ?

(c) Two isomeric α-halo ketones **A** and **B** on treatment with NaOMe (separately) gave the same product PhCH₂CO₂Me. Identify **A** and **B**.

Unit-III

5. (a) Analyse the following molecules retro synthetically and suggest plausible synthetic $2\frac{1}{2}+2\frac{1}{2}$ route to them.



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- (b) Give synthetic equivalent for the following species.
 - (i) +CH₂COCH₃

- (ii) +CH2CH2OH
- (c) Predict the major product of the following reaction with proper stereochemistry.

2

2

$$(R)$$
-PhCO-CHMeEt $\rightarrow (LiAlH_4/H_3O^+) \rightarrow ?$

(d) Which combination of reagents is appropriate for the following transformation?

1

6. (a) Synthesize the following compound using Diels-Alder reaction one of the key step.

2

(b) Explain with proper example: Illogical Nucleophile, Functional Group Addition.

3

(c) Show disconnection of hexane-2,4-dione in terms of consonant and dissonant polarities.

2

(d) Outline a synthesis of the following molecule showing logical retro synthetic analysis.

3

Unit-IV

7. (a) Concentrated solutions of C₂H₅OH and HOCH₂CH₂OH have broad O-H bands near 3350 cm⁻¹. On dilution with CCl₄, the spectrum of ethylene glycol does not change but that of the alcohol shows a sharp peak at 3600 cm⁻¹ replacing the band at 3350 cm⁻¹. Provide a suitable explanation in support of this observation.

3

(b) Arrange the following compounds in order of increasing carbonyl stretching frequencies with proper explanation.

2



(c) Calculate λ_{max} values for the following compounds using Woodward Fieser rule.

2+2

ii.

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(d) Compound B (C₃H₆Cl₂) displays the following spectroscopic data. 4 UV : $\lambda_{max}(\varepsilon_{max})$: Transparent above 210 nm IR (cm⁻¹): 2950, 1270, 690. ¹H-NMR : δ (ppm) 1.25 (d, 3H, J 7 Hz), 3.6 (m, 1H), 3.2 (dd, 2H, J 7 Hz, 11 Hz). Deduce the structure of compound B and explain the spectroscopic data as far as practicable. 2 (e) Toluene is oxidised to benzaldehyde. What changes would you expect in PMR spectral feature for the product with respect to that of the starting material? (f) Mention one solvent, other than CDCl₃, that acts as NMR-solvent. 1 8. (a) PhCOCH₃ gives two isomeric oximes. Both of them are separately treated with 3 conc. H₂SO₄ to give the products **A** and **B** respectively. Identify the products on the basis of IR spectroscopy. (b) An organic compound of molecular formula, C₉H₁₀O₂ showed three peaks in the 3 PMR spectrum as given below: δ 1.96, singlet, 3H; δ 5.0, singlet, 2H and δ 7.2, singlet, 5H. One of the intense IR bands of this compound appears at 1740 cm⁻¹. Deduce the structure of the compound and explain the spectral data. (c) Account for the following observations. 2+2+2Although sp carbon is more electronegative than sp² carbon, alkenyl protons appear at higher δ value than alkynyl protons in ¹H-NMR spectrum. (ii) Stretching of aldehydic C-H appears as a doublet and at higher wave number than alkenyl C-H. (iii) Homoannular dienes absorb at higher wavelength than heteroannular dienes. (d) 'C=C' stretching frequency of cyclobutene is at 1566 cm⁻¹ but that of 2 1-methylcyclobutene is at 1641 cm⁻¹. Account for this observation. (e) What is bathochromic shift in UV spectroscopy? Explain with a suitable example. 2 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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