

### WEST BENGAL STATE UNIVERSITY

B.Sc. Honours 4th Semester Examination, 2021

# CEMACOR10T-CHEMISTRY (CC10)

## **ORGANIC CHEMISTRY-IV**

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) Why ammonolysis on the corresponding alkyl bromides (RBr) cannot be used for the preparation of <sup>t</sup>BuNH<sub>2</sub> and Me<sub>3</sub>CCH<sub>2</sub>NH<sub>2</sub>? How would you prepare these amines from carboxylic acids (RCO<sub>2</sub>H)?

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(b) Give the product with plausible mechanism:

$$Me-N-CO_2Et \xrightarrow{KOH} ?$$

- 2. (a) Explain why benzene diazonium chloride couples with phenol in alkaline medium but not with anisole under the same reaction conditions.
  - (b) Give the product(s) of the following reaction with plausible mechanism:

$$\bigcirc O \xrightarrow{CH_2N_2} ?$$

(c) Identify A and B in the following:

$$Ph_2NH \xrightarrow{Li} A \xrightarrow{Phl} B$$

#### **Unit-II**

- 3. (a) In the Arndt-Eistert synthesis two equivalent of diazomethane is recommended. 2 Explain.
  - (b) Identify the product(s) in the following with plausible mechanism. 2+2

(i) 
$$H_2SO_4$$
  $H_2SO_4$  ? (ii)  $N=N$   $N=N$ 

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(c) Derive the product(s) of Baever-Villiger rearrangement on the following enantiomerically pure ketone. Suggest mechanism and comment on the stereochemistry of the product(s).

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2+2

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- 4. (a) Carry out the following conversion and suggest plausible mechanism (any *two*). 2+2
  - (i) Acetophenone to 2-phenylpropanal
  - (ii) Phenol to catechol
  - (iii) p-Hydroxyacetophenone to paracetamol.
  - (b) The isomeric pinacols Ph<sub>2</sub>C(OH)C(OH)Me<sub>2</sub> and PhMeC(OH)C(OH)PhMe undergo acid-catalyzed rearrangement to afford a common product. — Explain.
  - (c) Identify C and D with proper mechanistic explanation.

#### **Unit-III**

5. (a) Draw the scheme for retro-synthetic analysis of the following hydrocarbon using FGA strategy. Also, depict the synthetic pathway of it.

(b) Predict the major product of the following reaction with reason.

(R)-EtCOCH(Me) Bu<sup>t</sup> i) LiAlH<sub>4</sub> / THF 
$$\stackrel{\oplus}{\longrightarrow}$$
 ?

- (c) Explain with suitable examples: Synthon and illogical electrophile.
- 6. (a) Draw the structure of the major products (M and N) in the following reactions. 4 Establish the stereoisomeric relationship between M and N and rationalize the results.

i. Ph CHO 1. PhMgBr M ii. Ph Ph 1. LiAlH<sub>4</sub> N Me 
$$\frac{1. \text{LiAlH}_4}{2. \text{ aq. NH}_4 \text{Cl}}$$
 N

- (b) What do you mean by high dilution technique for the synthesis of large ring compounds? — Explain.
- (c) What do you mean by chemo-selective reaction? Give an example.

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(d) Write the products with proper stereochemistry. Justify your answer.

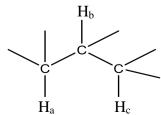
H NCH<sub>2</sub>Ph + MeLi 
$$\longrightarrow$$
 A + B CHO

#### **Unit-IV**

- 7. (a) Distinguish the following pair of compounds on the basis of their IR spectra: 2+2 (any *two*)
  - (i) Acetone and hexamethyl acetone
  - (ii) Salicylic acid and p-hydroxy benzoic acid
  - (iii) Phenyl acetate and methyl benzoate.
  - (b) The UV spectrum of mesityl oxide shows absorption bands at 321 and 230 nm in hexane. Assign them in terms of electronic transition. Depict the changes of this spectrum if the experiment is carried out in 95% ethanol solvent. Justify your answer.
  - (c) An organic compound of molecular formula  $C_6H_{12}O$  shows a peak at 1715 cm<sup>-1</sup> in its IR spectrum. The  $^1H$  NMR spectrum of the compound displays two singlets at  $\delta$  0.9 and 2.2 in the ratio of 3:1. Deduce the structure of the compound and explain the spectral data.
  - (d) "Two protons are chemically equivalent but magnetically non-equivalent". Justify the statement with an example.
  - (e) Predict the number(s) of <sup>1</sup>H-NMR peak of chlorocyclopropane and justify.
  - (f) Esters of o-chlorobenzoic acid show two C=O stretching frequencies. Explain.
- 8. (a) Distinguish the following pairs by UV spectroscopy (any *two*):
  - (i) p-cresol and anisole
  - (ii) mesity oxide and  $CH_2 = C(Me)CH_2COMe$
  - (iii) aniline and cyclohexylamine.
  - (b) Predict the organic compound of molecular formula  $C_9H_{10}O_2$  from the following spectral data.

IR:  $1740 \text{ cm}^{-1}$ ; <sup>1</sup>H NMR:  $\delta 1.96 (3\text{H, s})$ , 5.00 (2H, s) and 7.20 (5H, m).

- (c) The stretching absorption maxima for C–H and C–D are approximately 2900 cm<sup>-1</sup> 2 and 2200 cm<sup>-1</sup> respectively. Explain why.
- (d) Draw the splitting pattern for H<sub>b</sub> in the <sup>1</sup>H-NMR spectrum of the fragment given below, where
  - (i)  $J_{ba} = 12 \text{ Hz}$  and  $J_{bc} = 6 \text{ Hz}$  (ii)  $J_{ba} = 12 \text{ Hz}$  and  $J_{bc} = 12 \text{ Hz}$ .



(e) Define the terms (i) up-field (ii) downfield shifts as used in NMR spectroscopy.

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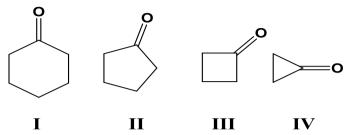
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- (f) The UV absorption maxima of aniline in aqueous solution are different from those of benzene, but the positions of UV absorption maxima of aniline in acidic solution (pH  $\simeq$  1) are almost identical with benzene. Explain.

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(g) Arrange the following compounds according to their increasing order of 'C=O' stretching frequency and give reason.



**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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