

## WEST BENGAL STATE UNIVERSITY

B.Sc. Honours 4th Semester Examination, 2022

# 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) How would you chemically distinguish the following pair of compounds?
  - (i) Benzyl cyanide and benzyl isocyanide
  - (ii) N-methylaniline and N, N-dimethylaniline.
  - (b) Explain the products [A] and [B] with proper mechanism of the reaction.

$$CH_3CH_2NO_2 \xrightarrow{\text{aqueous}} [A] \xrightarrow{\text{50\% H}_2SO_4} [B]$$

- (c) How can you prepare N-methylaniline from aniline?
- 2. (a) Suggest the product(s) and give the mechanism for the following reaction:

$$Et_2NH \xrightarrow{\text{HCHO} / \text{HCOOH}} \text{Product(s)}$$

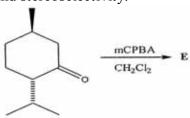
(b) Give the structures of [C] and [D]:

(i) 
$$\frac{\text{LiAlH}_4 \text{ / Ether}}{\text{H}_3\text{O}^+}$$
 [C]

(c) How can you convert aniline to 1,3,5-tribromobenzene?

## **Unit-II**

3. (a) Draw the structure of **E** with the proper configuration of the stereogenic centres and give plausible mechanistic steps. Discuss the effect of stereoelectronic factors for the determination of regio and stereoselectivity.



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- (b) Carry out the following conversions:
  - (i) Phthalic anhydride anthranilic acid
  - (ii) p-Cresol Me
- 4. (a) Outline two methods for the preparation of phenyl acetate. Rationalise the products in the reaction of phenyl acetate and anhydrous AlCl<sub>3</sub> (Friedel-Crafts conditions) with plausible mechanism. Explain the role of solvents and temperature in the control of product ratio.
  - (b) Convert benzoyl chloride to phenylacetic acid in one-step. Suggest plausible 2 mechanism with a comment on the intermediate.

2+2

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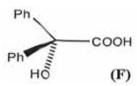
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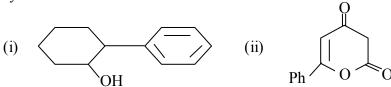
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(c) Convert benzoin to the α-hydroxyacid (F) in two steps and suggest plausible mechanism for step two only.

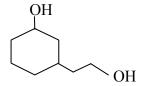


## Unit-III

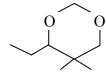
- 5. (a) Give the synthetic equivalent for the following species:
  - (i) R (ii) Q (iii) Q (iv)  $\overline{C}O_2H$
  - (b) Show the retrosynthetic analysis of the following compounds and then carry out the  $1\frac{1}{2}+1\frac{1}{2}$  synthesis:



(c) Plan a retrosynthesis followed by the synthesis of the following by FGI approach.



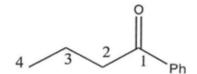
(d) Propose a synthesis of the following compound:



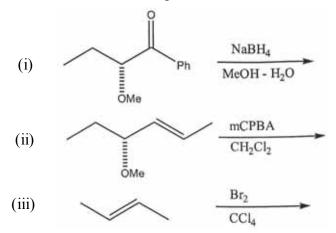
6. (a) Depict the disconnections, as indicated for the retrosynthesis of the following ketone and then draw the synthons and the corresponding synthetic equivalents.

Also, classify all the synthons as logical / illogical and donor / acceptor terminology.

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- (i) FGI followed by C C disconnection
- (ii) 1,2 C C disconnection
- (iii) 2,3 C C disconnection
- (iv) 3.4 C C disconnection.
- (b) Predict the product(s) in the reactions given below and comment whether these are stereoselective or stereospecific reactions.



(c) Carry out the following conversions using protection / deprotection strategy.

(i)  $CO_2Et$   $CH_2OH$   $CH_2OH$ 

## <u>Unit-IV</u>

- 7. (a) Sketch and label the possible bending vibrational modes in CH<sub>2</sub>Cl<sub>2</sub>.
  - (b) What are the radiation sources of IR spectrometer and UV spectrometer?
  - (c) What are the significance of the terms: (i) absorbance and (ii) vacuum UV?
  - (d) Describe Fermi coupling. Which region in IR spectrum is known as fingerprint region? Describe its significance.
  - (e) Distinguish the following pair of compounds using spectroscopy:

(i) 
$$\bigcirc$$
O and  $\bigcirc$ O (IR spectroscopy)

- (ii) cis and trans stilbene (UV spectroscopy)
- (iii)  $CH_3 CH_2 C \equiv CH$  and  $H_3C C \equiv C CH_3$  (<sup>1</sup>H NMR)
- (f) Aromatic protons are more deshielded than ethylenic protons, although both the types of protons are attached to sp<sup>2</sup> hybridised C-atom. Explain.

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(g) An organic compound having molecular formula C<sub>8</sub>H<sub>7</sub>NO<sub>3</sub> shows a strong IR bond 3 at 1690 cm<sup>-1</sup> and three signals at  $\delta$  8.5 (doublet)  $\delta$  7.9 (doublet)  $\delta$  2.5 (singlet) in its <sup>1</sup>H NMR spectra. Establish the structure of the compound. 8. (a) In IR spectroscopy ethylacetoacetate shows the peaks at 1715 cm<sup>-1</sup>, 1690 cm<sup>-1</sup>, 2 2900 cm<sup>-1</sup> and 3500 cm<sup>-1</sup>. How will you explain it? 2 (b) Define the following terms: (ii) Hypsochromic effect (i) Hypochromic effect, (c) How would you distinguish 4-nitro-N,N-dimethylaniline and acidified 4-nitro-N,N-2 dimethylaniline by UV spectroscopy? (d) Predict and label the chemical shifts in  $\delta_{ppm}$  and the splitting pattern of the 3 nonequivalent Hs of butanone. Express the difference of chemical shift value in Hz between the upfield and downfield Hs in butanone. (e) The compound (X) is obtained as major product after the mononitration of toluene. 2 Compound X on reduction with Sn and concentrated HCl gives compound Y. Compare the <sup>1</sup>H-NMR spectra of X and Y. (f) What are the two probable products (enone) in the aldol condensation of acetone? 3 How would you distinguish them by UV, IR and <sup>1</sup>H-NMR spectroscopy? (g) Why is tetramethylsilane (TMS) preferred as an internal standard in <sup>1</sup>H-NMR 2 experiment?

**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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