Reg. No. : $\qquad$
Name : $\qquad$

Third Semester M.Sc. Degree Examination, February 2024
Chemistry / Analytical Chemistry / Polymer Chemistry CH 232 / CL 232 / PC 232 : ORGANIC CHEMISTRY - III
(2020 Admission Onwards)
Time : 3 Hours

## SECTION - A

Answer two among (a), (b) and (c) from each. Each sub question carries 2 marks.

1. (a) Among the following dienes which one will observe at lower wavelength? Why?


(b) An intense peak at m/e: 149 is observed in the mass spectrum of diethyl phthalate. Account for this.
(c) Two $\gamma$ - lactones having double bond give absorption at $1800 \mathrm{~cm}^{-1}$ and $1750 \mathrm{~cm}^{-1}$. Write the structure and assign the value for each compound.
2. (a) An organic compound molecular formula $\mathrm{C}_{4} \mathrm{H}_{9} \mathrm{NO}$ shows ${ }^{1} \mathrm{H}-$ NMR peaks at $\delta(\mathrm{ppm}): 2.9(\mathrm{t}, 4 \mathrm{H}), 3.8(\mathrm{t}, 4 \mathrm{H}), 1.8($ broad $\mathrm{s}, 1 \mathrm{H})$ assign a suitable structure.
(b) The ${ }^{13} \mathrm{C}$-NMR spectrum of one of the butyl acetate isomers $\left(\mathrm{C}_{4} \mathrm{H}_{9} \mathrm{OCOCH}_{3}\right)$ shows signal at $\delta c 22,28,80$ and 170 what is its structure? (Intensity of peak at $\delta c 28$ much more intense than that $\delta c 22$ )
(c) Predict the chemical shift position for the protons in 4-nitroanlsole.
3. (a) Complete the following:
(i) $\mathrm{Ph} \mathrm{CH}=\mathrm{CHCoPh}+\mathrm{CN}^{\ominus} \xrightarrow{\text { weak base }}$ ?
(ii) $\mathrm{CH}_{3} \mathrm{CH}=\mathrm{CH}-\mathrm{COCH}_{3} \xrightarrow[\mathrm{H}_{2} \mathrm{O}, \mathrm{H}^{+} \text {,Strongbase }]{\mathrm{CH}_{3} \mathrm{MgI}}$
(b) Predict the structure of product $A$ and $B$ in the reaction given below.

(c) Predict the product in the following :

4. (a) Give any two protecting groups for phenols.
(b) Suggest a retro synthetic route for the following compounds.

(c) Why cyanide ions $\left(\mathrm{CN}^{-}\right)$is a highly specific catalyst for the benzoin condensation?
5. (a) What is Jones oxidation reaction?
(b) Illustrate the use of borohydride for the transformation of isopropanol to $n$-propanol.
(c) Write the main product of reaction between o-dichlorobenzene and sodamide.

## SECTION - B

Answer either (a) or (b) from each question. Each sub question carries 5 marks.
6. (a) Write all Possible isomers of molecular formula $\mathrm{C}_{6} \mathrm{H}_{6} \mathrm{O}$ whole UV band exhibit at $\lambda \max 187 \mathrm{~nm}$ (high intensity) and at $\lambda$ max 280 nm with low intensity.
(b) Show the mass fragmentation pattern of 3-Methyl pyridines.
7. (a) Assign the structure of the compound on the basis of spectral data. UV $\lambda$ max : No band above 200 nm ; IR : v max : $1740 \mathrm{~cm}^{-1}$
${ }^{1} \mathrm{H}$ NMR $\delta=4.0(\mathrm{t}, 2, \mathrm{H}) ; 2.2(\mathrm{~m}, 2 \mathrm{H}) ; 2.3(\mathrm{~m}, 1 \mathrm{H}): 1.15(\mathrm{~s}, 3 \mathrm{H})$
(b) Write a note on shift reagent in NMR spectroscopy.
8. (a) What is Gillman reagent? How it's formed? Complete the following.

(b) Write a note on 1,2 and 1, 4- enone addition reactions.
9. (a) Explain stork enamine acylation reaction. Outline its mechanism.
(b) What is Umpolung? Explain.
10. (a) How is Tri-n-butyl tinhybride $\left((n-B u)_{3} \mathrm{Sn}_{4}\right)$ prepared where it is used in the field of organic group transformation; Explain it with suitable examples.
(b) Explain Birch reduction. Complete the following with mechanism.


## SECTION - C

Answer any three questions. Each question carries 10 marks.
11. (a) Explain the El in mass spectroscopy.
(b) Summarize the general trends of structural variation on the position of carbonyl stretching frequency in IR spectra.
12. Three isomeric compound, $\mathrm{C}_{4} \mathrm{H}_{8} \mathrm{O}_{3}$ give the following ${ }^{1} \mathrm{H}$ spectra. Deduce the possible structure for them.

Compound $1: \delta 1.3$ (t, 3H, J = 7 Hz ); 3.6 (q, $2 \mathrm{~Hz}, \mathrm{~J}=7 \mathrm{~Hz}$ ); 4.15 (s, 2 H ); 12.1 (s, 1H) ppm.

Compound 2 : 1.2 (d, 3H, J-7 Hz); 2.3 (d,2 H,J = 7 Hz ); 4.15 (1:5:10:10:5:1 sextet, $1 \mathrm{H}, \mathrm{J}=7 \mathrm{~Hz}$ ) ppm (Spectrum run in $\mathrm{D}_{2} \mathrm{O}$ )

Compound 3:3.5 (s, 3H); 3.8 (s, 3H) 4.08 (s, 2H) ppm
13. Write notes on :
(a) Silane carbanion and its reaction.
(b) Alkynyl Cu (I) reagents.
14. Explain the following :
(a) Creation of cis and trans double bonds.
(b) Stepens-Castro coupling reactions.
15. Give a brief account on application of following reagents in organic synthesis.
(a) $\mathrm{OsO}_{4}$
(b) DIBAL-H

