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H – 4110

Reg. No. :

Name :

Third Semester M.Sc. Degree Examination, January 2020

Chemistry/Polymer Chemistry

CH/CL/CM/CA/ PC 232 : ORGANIC CHEMISTRY-III

**(Common for Chemistry (2016 Admission Onwards) and Polymer Chemistry
(2018 Admission))**

Time : 3 Hours

Max. Marks : 75

SECTION – A

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

- Compare the relative red shifts of p-nitroaniline and p-diaminobenzene.
 - Predict the relative IR absorption values (approximate) due to C=O stretch in an aldehyde, ketone and amide.
 - Give any two major peaks and the mode of their formation in the mass spectrum of ethyl benzoate.
- The NMR spectrum of dimethyl formamide at room temperature shows two peaks for its methyl groups. Why?
 - Write the advantages of the 2D NMR technique, COSY.
 - Why are acetylenic hydrogens more up-field than vinylic hydrogens?

P.T.O.



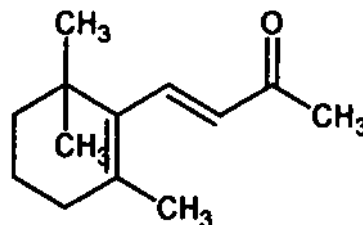
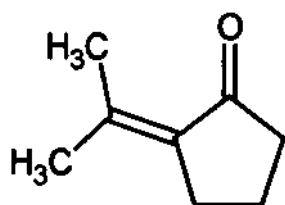
3. (a) Give the reagent and conditions for the selective conversion of an α, β -unsaturated ketone to the respective alcohol.
- (b) Write the mechanism of carbon-carbon bond formation between an alkene and an alkyl halide using palladium catalyst.
- (c) Explain an application of HI/O_4 in organic synthesis.
4. (a) Write the method of conversion of acetaldehyde to acetone using *umpolung*.
- (b) Explain the term combinatorial synthesis.
- (c) What is Mitsunobu reaction?
5. (a) Differentiate between "Gradient Elution" and "Isothermal Elution" in chromatography.
- (b) What is the principle of capillary zone electrophoresis?
- (c) Why liquid chromatography is a viable technique for the separation of proteins, nucleosides etc., as compared to gas chromatography?

(2 × 10 = 20 Marks)

SECTION – B

(Answer **either (a) or (b)** from each question. Each sub question carries **5** marks)

6. (a) (i) By using Woodward Fieser rules calculate the λ_{max} values for the following compounds.



- (ii) Which has a lower characteristic stretching frequency, the C-H or C-D bond? explain briefly.



- (b) (i) What are the predicted m/z values (masses) and relative heights of all the molecular ions of 1-bromoethane that would appear on a mass spectrum (excluding peaks produced by ^{13}C and ^2H)?
- (ii) Write short notes on metastable ions
7. (a) What is anisotropic effect? Explain the paramagnetic anisotropy of alkene, aldehydic and aromatic protons.
- (b) Predict the number of signals and their chemical shift and spin-spin coupling in each of the following compounds in ^1H NMR spectra.
- (i) $\text{CH}_3\text{-CH}_2\text{-Cl}$
- (ii) $\text{CH}_3\text{-CH(Cl)-CH}_3$
- (iii) $\text{Br-CH}_2\text{-CH}_2\text{-CH}_2\text{-Br}$
8. (a) What is an enamine? How it is prepared? Give two synthetic applications.
- (b) With suitable examples (two), illustrate the application of Peterson olefination in stereoselective synthesis of alkenes.
9. (a) Explain the details of Sharpless asymmetric epoxidation of allylic alcohols.
- (b) Write short note on
- (i) Electrochemical Kolbe oxidation
- (ii) Olefin metathesis.
10. (a) Explain the development of TLC plates. How do you choose the solvents for the development of TLC plates?
- (b) Discuss the affinity and chiral separations using HPLC.

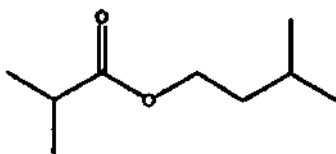
(5 × 5 = 25 Marks)



SECTION – C

(Answer **any three** questions. Each question carries **10** marks)

11. Describe briefly the major ion production techniques in mass spectrometry.
12. (a) Draw the proton decoupled ^{12}C -NMR, DEPT-45, 90 and 135 spectra of given compound. **4**



- (b) Write notes on
- (i) Shift reagents
 - (ii) HMBC 2D NMR spectra. **6**
13. Write notes on the following
- (a) Mannich reaction
 - (b) Wolf-Kishner reduction
 - (c) Shapiro reaction
 - (d) Suzuki coupling
14. Discuss the advantages and disadvantages of hydroxyl, thiol, carboxyl, and carbonyl protecting groups used in organic synthesis.
15. Explain the applications of Gas chromatography in separation, identification and quantitative analysis of organic compounds

(3 × 10 = 30 Marks)

