

Seat No. : _____

ZO-127

May-2014

M.Sc., Sem.-II

408 : Chemistry

(Organic Chemistry)

Time : 3 Hours]

[Max. Marks : 70

- Instructions :** (1) All questions are compulsory.
(2) Figures to right indicate full marks.

1. Answer the following :

- (a) (i) Write a note on high resolution mass spectroscopy. 7
(ii) Give any three differences between ^{13}C NMR and ^1H NMR spectra.

OR

- (i) Explain how mass spectra are useful in detecting the presence of an atom Br, Cl, I in molecule.
(ii) Write a note on factors (electro negativity and hybridization of carbon) affecting in ^{13}C chemical shift.
(b) On the basis of following spectral data, deduce the structure of the compound with suitable explanation : 7

Molecular weight – 108

UV – λ_{max} 273 ($\log \epsilon = 3.3$)

IR – 3435 (b), 3075 (m), 2955(m), 1650 (m), 1595(s), 1498 (s), 1250(s), 885(s).

^1H NMR – 2.2 (s, 3H), 4.91 (s, 1H), complex 6.85 (4H)

Mass – 109, 108, 107, 91, 80, 79, 77

OR

On the basis of following spectral data, deduce the structure of the compound with suitable explanation.

Molecular weight-126

IR (cm^{-1}) – 3050, 2950, 1720, 1600, 1440, 1300

^1H NMR – 3.8 (s, 3H), 6.5 (dd, 1H), 7.1 (dd, 1H), 7.5 (dd, 1H).

Mass – 126, 95, 67, 39

^{13}C NMR – 51, 110, 117, 145, 147, 160

2. Answer the following :

- (a) (i) Draw Jablonski diagram and explain the terms-fluorescence and phosphorescence. 7
(ii) Explain Norrish type-II reaction.

OR

- (i) Explain Di-Π methane rearrangement with two supporting evidences.
(ii) On the basis of molecular orbital structure of a carbonyl group, explain photo reduction of benzophenone in the presence of toluene.
(b) Give one synthesis and two importance reactions for Imidazole and Quinazoline. 7

OR

Give one synthesis and two important reactions for Thiazole and Pyrimidine.

3. Answer the following :

- (a) (i) What is Mannich base ? Discuss mechanism for the generation of Mannich base through acid and base catalyzed reaction with relevant sequential steps. 7
(ii) Give a brief account on Suzuki reaction.

OR

- (i) What is Ylide ? How phosphine ylides are prepared ? Discuss the application of phosphorous ylides in Wittig reaction.
(ii) Give a brief account on Sonogashira reaction.
(b) (i) What is Stobbe condensation ? Give sequential step, discuss conversion of cyclohexanone to 3-cyclohexyl propanoic acid. 7
(ii) Give a brief account on Birch reduction.

OR

- (i) What is Knoevenagel condensation ? Give complete mechanism of Knoevenagel condensation with one application.
(ii) Give a brief account on Mitsunobu reaction.

4. Answer the following :

- (a) (i) What is Phase transfer catalyst ? Describe how crown ether acts as the catalyst in the oxidation reaction using KMnO_4 . 7
(ii) Give brief account on application of Baker yeast in organic synthesis.

OR

- (i) What is DCC ? Give an account on application of DCC in peptide synthesis.
(ii) Give brief account on application of DIBAL-H in organic synthesis.

- (b) Discuss selectivity, mechanism and utility of the following reagents : 7
- (i) Grignard reagent
 - (ii) n-Butyl lithium

OR

Discuss selectivity, mechanism and utility of the following reagents :

- (i) Lithium diisopropyl amide (LDA)
- (ii) Gilman's reagent – Lithium dimethyl cuprate.

5. Answer the following : 14

- (i) Most abundant peak for toluene appears at m/e 91. – Explain.
 - (ii) The δ ppm values of each proton in 2-propane are 0.92, 1.60, 2.41 and 2.13. Write structure and assign values against each proton.
 - (iii) How cis-stilbene and trans-stilbene are distinguished from ^1H NMR ?
 - (iv) Explain ortho effect in mass spectroscopy.
 - (v) Explain Photosensitization.
 - (vi) How Oxetane is generated from ketone and alkene ?
 - (vii) Give one synthesis of Oxazole.
 - (viii) Give structures of the following compound :
 - (i) 1, 4-thiazine
 - (ii) Cis-2, 4-dimethyl thietane
 - (ix) Write structure of Dess-Marlin periodinane with one application.
 - (x) What is Swern oxidation ?
 - (xi) Name the reagents and their function to carry out Vilsmeier Haack reaction.
 - (xii) Which ingredients are used in Michael addition ?
 - (xiii) By which reagent electrophile can be converted to nucleophile and nucleophile can be converted to electrophile ?
 - (xiv) What is DDQ ? Give one application of DDQ.
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