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Code No.: 5412 Sub. Code: ZCHM 21

M.Sc. (CBCS) DEGREE EXAMINATION, APRIL 2023.

Second Semester

Chemistry - Core

STEREOCHEMISTRY, ORGANIC REAGENTS AND PHOTOCHEMISTRY

(For those who joined in July 2021 onwards)

Time: Three hours

Maximum: 75 marks

PART A - (10 × 1 = 10 marks)

Answer ALL questions.

Choose the correct answer:

- 1. Which among the following is a prochiral molecule?
 - (a) Lactic acid
- (b) propionic acid
- (c) acetic acid
- (d) tartaric acid
- 2. Biphenyl exhibits -
 - (a) constitutional isomerism
 - (b) stereoisomerism
 - (c) atropisomerism
 - (d) topomerism

- 3. Preferred conformation of 1,2-dichlorocyclohexane is
 - (a) cis-e, a
- (b) cis-a, e
- (c) trans e, e
- (d) trans a, a
- 4. Which is the most stable conformation of cis-1,4-di-t-butylcyclohexane
 - (a) chair

- (b) boat
- (c) twist boat
- (d) gauche
- 5. IBX oxidizes toluene to -
 - (a) benzoic acid
 - (b) benzyl alcohol
 - (c) benzophenone
 - (d) benzaldehyde
- 6. The reagent used for the following conversion

$$\underset{\mathsf{H}}{\overset{\mathsf{R}_2}{\longrightarrow}}\underset{\mathsf{R}_1}{\overset{\mathsf{O}}{\longrightarrow}}\overset{\mathsf{OH}}{\longrightarrow}+\overset{\mathsf{O}_{\mathsf{L}_1}}{\overset{\mathsf{R}_2}{\longrightarrow}}$$

- (a) Lemieux-Johnson reagent
- (b) Lemieux-Von Rudloff reagent
- (c) Luche reagent
- (d) Fetizon's reagent

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- 7. Di-pi methane rearrangement involves _ intermediate
 - (a) carbonium ion
- (b) carbanion
- (c) carbene
- (d) biradical
- 8. _____ reaction involves δ -H transfer
 - (a) Paterno-Buchi
- (b) Mc Lafferty
- (c) Barton
- (d) di-pi methane
- 9. Claisen rearrangement is
 - (a) 1,3-Sigmatropic reaction
 - (b) 3,3-Sigmatropic reaction
 - (c) 1,5-Sigmatropic reaction
 - (d) 1,7-Sigmatropic reaction
- 10. The reaction shown is a/an reaction





- (a) electrocyclic
- (b) cycloaddition
- (c) sigmatropic
- (d) cheletropic

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PART B — $(5 \times 5 = 25 \text{ marks})$

Answer ALL questions, choosing either (a) or (b). Each answer should not exceed 250 words.

11. (a) Explain Cram's chelation model with an example.

Or

- (b) Discuss asymmetric synthesis using enzymes.
- 12. (a) Analyze the conformations of 1,2-disubstituted cyclohexane and explain related properties.

Or

- (b) Draw the most stable conformation for following molecules and explain why?
 - (i) trans-1,2-diclorocyclohexane
 - (ii) cis-1,3-dihydroxycyclohexane
- 13. (a) Compare the mechanism and stereochemistry of Woodward and Prevost hydroxylation.

Or

(b) Discuss the speciality of 1,3-dithiane in Umpolung synthesis.

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[P.T.O.]

14. (a) Briefly discuss Norrish Type I and Type II reactions

Or

- (b) Write a short note on cis-trans isomerization.
- (a) Thermal cyclisation of 1,3-butadiene is a conrotatory process. Substantiate using FMO method.

Or

(b) Using FMO method discuss the stereochemistry of 1,5-sigmatropic migration.

PART C — $(5 \times 8 = 40 \text{ marks})$

Answer ALL questions, choosing either (a) or (b) Each answer should not exceed 600 words.

16. (a) Giving examples differentiate stereospecific and stereoselective synthesis.

Or

- (b) Explain how allenes and spiranes exhibit optical isomerism though they do not have asymmetric atoms.
- 17. (a) Discuss the various conformations and properties of perhydrophenanthrene.

Or

(b) State Curtin-Hammett principle. Briefly discuss two applications.

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- 18. (a) How are the following used in organic synthesis?
 - (i) Merrifield resin (ii) Vaska's catalyst

Or

- (b) Write short notes on (i) Gilman's reagent (ii) Luche reagent
- 19. (a) Explain (i)quantum efficiency (ii) Paterno-Buchi reaction.

Or

- (b) Write short notes on (i) Jablonski diagram (ii) Di-pi methane rearrangement
- (a) Using correlation diagram method discuss the stereochemical course of 4+2 cycloaddition.

Or

(b) Write short notes on (i) Cope rearrangement(ii) Fluxional tautomerism

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