 LOYOLA COLLEGE (AUTONOMOUS), CHENNAI – 600 034

**M.Sc.** DEGREE EXAMINATION - **CHEMISTRY**

THIRD SEMESTER – NOVEMBER 2012

# CH 3808 - PHOTOCHEMISTRY AND ORGANIC SYNTHESIS

Date : 01/11/2012 Dept. No. Max. : 100 Marks

Time : 9:00 - 12:00

**Part-A**

Answer **ALL** questions: (10 × 2 = 20)

01. How is diborane specific in its reactivity towards substituted alkenes?

02. Draw the FMO picture of the excited state HOMO of 1,3,5-hexatriene.

03. What are regioselective reactions? Give an example.

04. What are the products formed when ethyl bromide is reduced electrochemically on platinum electrode?

05. Predict the stereochemistry of the product.



06. What is Fries photochemical rearrangement? Write the mechanism of the reaction.

07. What are the synthons prepared from the following synthetic equivalents?

a) 2-bromobutane b) acetyl chloride

08. What is the geometry of excited state ethylene molecule? Give reasons.

09. What are group transfer reactions? Give examples.

10. What is oxy-Cope rearrangement reaction? Give an example.

**Part-B**

Answer any **EIGHT** questions: (8 × 5 = 40)

11. Why Wittig Horner reaction is preferred to Wittig reaction? Mention the advantages of the Wittig Horner reaction with an example.

12. Explain the synthesis of following difunctionalised compounds.

a) 1,3-propanediamine b) ethyl acetoacetate

13. How are protection, activation and attachment of bridging group done repeatedly in the synthesis of a polypeptide?

14. Explain the mechanism of following reactions.

a) oxidation of an 2-butene by KMnO4 in basic medium.

b) Wolff Kishner reduction of acetophenone

15. Write the complete mechanism of electroreduction of nitrobenzene.

16. Perform retrosynthetic analysis and suggest a suitable synthetic method of the following. (3 + 2)

 

17. Draw correlation diagram for the electrocyclization of 1,3-butadiene by con rotation. Predict whether the reaction is thermally or photochemically allowed.

18. If hydrazobenzene in acid medium undergoes (3,3)- and (3,5)-sigmatropic rearrangements, what are the products formed? Explain the mechanism of the reaction.

19. Explain the mechanism of the following reaction and predict the stereochemistry of the mentioned H atoms in the product.



20. What is Barton reaction? How does it take place in steroids? Explain with an example.

21. How does 4,4-diphenylcyclohex-2-en-1-one undergo Zimmerman rearrangement to form various photochemical products?

22. Explain the Norrish type-I and type-II reactions with an example each.

**Part-C**

Answer any **FOUR** questions: (4 × 10 = 40)

23. a) Write the stereochemical importance of Stobbe reaction. (2)

b) Explain 1,2- and 1,4-Michael addition reactions. (5)

c) How unnatural synthons are used to prepare 1,2-difunctionalised compounds? Explain with an example. (3)

24. a) How are C-C disconnections done? Explain any four guidelines. (6)

b) Perform retrosynthetic analysis and suggest a suitable synthetic route to the following compound (4)



25. a) Explain protection and deprotection of an amine. (4)

b) Explain the mechanism of the following reactions with examples. (3+3)

i) NaBH4 reduction of an imine ii) Peracid oxidation

26. a) Explain the synthesis of cubane. . (5)

b) How mercuric acetate acts as a dehydrogenating agent? Explain with any two examples. (5)

27. a) Predict a suitable mechanism for the following thermal reaction. (4)



b) Discuss the FMO interactions in the 1,3-, and 1,5-sigmatropic rearrangement reactions. How is the stereochemistry altered in the product? (6)

28. a) Explain photoisomerisation reaction of stilbene. How is the process controlled by photosensitizers? (6)

b) Explain the di-π-methane rearrangement reaction with an example. (4)

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