

LOYOLA COLLEGE (AUTONOMOUS), CHENNAI – 600 034

M.Sc. DEGREE EXAMINATION – CHEMISTRY

THIRD SEMESTER – APRIL 2010

CH 3808 / 3800 - PHOTOCHEMISTRY AND ORGANIC SYNTHESIS

Date & Time: 26/04/2010 / 1:00 - 4:00 Dept. No.

Max. : 100 Marks

PART-A

Answer **ALL** questions.

(10 × 2 = 20)

01. What are the effects of reagents and solvents in Stobbe reaction? Give examples.
02. How is carbene synthesized? In what form it is used in reactions? Give an example.
03. Identify any two types of 1,3-dipolar compounds used for cycloaddition reactions. Give an example.
04. Draw the FMO orbital diagram of 1,3,5-hexatriene for thermal electrocyclic reaction.
05. Why group transfer reactions are neither cycloaddition nor sigmatropic rearrangement reactions?
06. Does hydroboration of alkene follow Markonikov's addition? Justify your answer with suitable example.
07. How is catalytic hydrogenation different from dissolving metal reduction? Give reasons.
08. What are natural synthons? Give suitable examples.
09. What are protecting groups? How is carbonyl protected and deprotected?
10. What are regiospecific control elements?

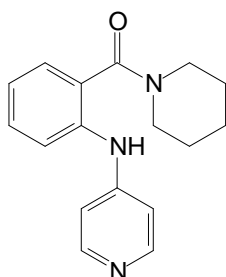
PART-B

Answer any **EIGHT** questions.

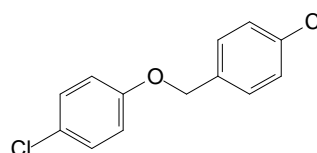
(8 × 5 = 40)

11. Write the mechanism of Simmon-Smith reaction.
12. Write a short note on aldol and crossed aldol condensation reactions. (5)
13. What are donor and acceptor synthons. Explain Umpolung concept of seebach?
14. How the following compounds can be disconnected to get suitable synthons?

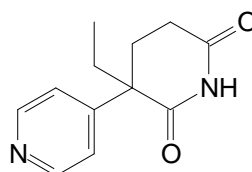
a)



b)

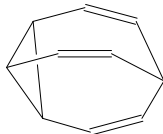


15. Perform retrosynthesis and subsequently synthesize the given compound.



16. Explain electro organic reduction with any two examples.
17. Explain the mechanism of following reactions.
 - a) Reformatsky reaction
 - b) Hydroboration reaction

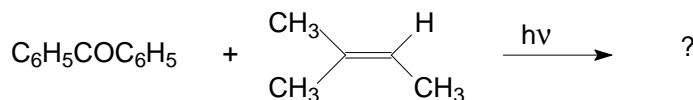
18. How is degenerate sigmatropic rearrangement explained in the following compound?



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

20. Explain the Barton reaction in steroidal compounds.

21. Explain the photochemical reaction in the following compound and predict the products.



22. Explain di- π -methane rearrangement with an example.

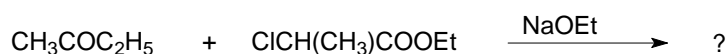
PART-C

Answer any **FOUR** questions.

(4 × 10 = 40)

23. a) Explain the mechanism of Wittig Horner reaction? What are the advantages of this method? How is the formation of intermediate confirmed? (5)

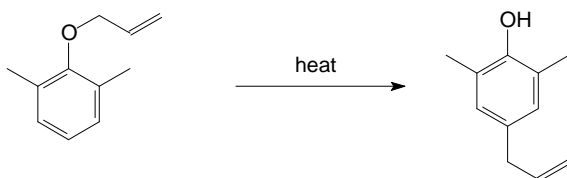
b) Predict the product and explain the mechanism of following reaction. (5)



24. a) Explain the mechanism of cycloaddition of isoprene with acrylic acid and predict the stereochemistry of the major product.

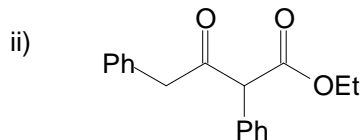
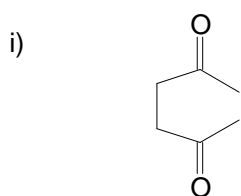
b) What is Alder's endo rule? How does it control the stereochemistry of cycloaddition product? Explain with an example.

25. a) There are two rearrangements involved in the following reaction. Identify them and write the mechanism.



b) How C-C disconnections are made in 1,3- and 1,4-difunctionalised compounds. Explain with an example each.

26. a) Describe a suitable synthetic strategy to the following.



b) Why alcohols are considered as good starting materials to synthesize various monofunctionalized compounds? Explain with a scheme. (5)

27. Briefly account for the following with necessary points.

a) SeO_2 oxidation of benzylic carbon is preferred to allylic carbon.

b) Birch reduction of toluene does not involve ipso attack.

c) Wolf Kishner reduction does not result in alcohols but CH_2 group.

28. a) Explain the photochemistry of α,β -unsaturated compounds with atleast two examples.

b) What is photoisomerisation? How does it vary with respect to various photosensitizers used?

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