LOYOLA COLLEGE (AUTONOMOUS), CHENNAI - 600 034



M.Sc. DEGREE EXAMINATION - CHEMISTRY

FOURTH SEMESTER - APRIL 2016

CH 4813 - ORGANIC SYNTHESIS & PHOTO CHEMISTRY

Date: 15-04-2016 Dept. No. Max. : 100 Marks
Time: 09:00-12:00

Part-A

Answer ALL questions.

 $(10 \times 2 = 20)$

- 1. HBr addition to propene is a regiospecific reaction-Justify.
- 2. How is positive charge at the β -carbon stabilized in organosilicon compounds?
- 3. Write the mechanism for the reduction reaction of 2-butyne with Na/liq. NH₃.
- 4. Give any two methods of preparation of dicyclohexylcarbdiimide (DCC).
- 5. How is convergent synthesis superior over linear synthesis?
- 6. Write the mechanism of SeO₂ oxidation of toluene.
- 7. What are group transfer reactions? Give an example.
- 8 Draw FMO picture of two molecules of 1,3-butadiene undergoing photochemical cycloaddition reaction.
- 9. What is photoisomerization reaction? Mention the factors affecting it.
- 10. What is a hot ground state reaction? Mention its salient features.

Part-B

Answer any EIGHT questions.

 $(8 \times 5 = 40)$

- 11. Explain the use of FGI in retrosynthetic analysis of (a) 1-phenylpropene and (b) N-ethylethanamine.
- 12. Give the applications of propan-1,3-dithiol as a protecting group.
- 13. Explain the use of silyl reagent as protecting group for alcohols.
- 14. Give the mechanism for the DCC and DMAP (cat.) mediated esterification reaction.
- 15. Explain the Starks extraction mechanism of phase transfer catalysis.
- 16. Identify A, B, & C in the following reaction.

$$\begin{array}{c|c}
OH & \xrightarrow{TsC1/Py} & A \xrightarrow{Hg(OAc)_2/H_2O} & B \xrightarrow{NaH} & C\\
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- 17. Write the complete mechanism of electroreduction of nitrobenzene.
- 18. (a) How is an aldehyde converted into an acid by Cr(VI) oxidation? Write the mechanism of the same.
 - (b) What is reductive amination reaction?
- 19. Draw the correlation diagram for the electrocyclization of 1,3,5-hexatriene by disrotation. Predict whether the reaction is thermally or photochemically allowed.
- 20. Explain cationic and anionic cycloaddition reactions with suitable example.
- 21. Write the mechanism of photochemical rearrangement of 2,4,6-octatrienone.
- 22. (a) Explain the photochemistry of α,β -unsaturated compounds with an example.
 - (b) Write the Paterno-Buchi reaction for alkyne derivative.

Part-C

Answer any FOUR questions.

 $(4 \times 10 = 40)$

- 23 a. What are stereospecific and stereoselective reactions? Give suitable examples.
 - b. Predict the synthons and synthetic equivalents for the following compounds.

- 24a. Explain the use of dithianes in the conversion of propargyl ketone into 1-phenyl acetyl acetone.
 - b. Give the reaction of diazomethane with (a) cyclopropylacetic acid and (b) CH₃COCl.
- 25 a. Write a note on the stereochemistry of Wittig reaction.
 - b. Illustrate with an example, the use of protection and deprotection of aldehydes and amine functional groups in organic synthesis.
- 26a. Write the mechanism of lead tetraacetate oxidization of a vicinal diol and a geminal-dicarboxylic acid.

(3+3)

b. Explain the LiAlH₄ reduction of propionamide.

(4)

27 a. Establish a suitable mechanism for the following reactions.

(3+3)

- a) 180 °C H
- b) MeS O H H Ph
- b. Explain degenerate sigmatropic rearrangement reaction using bullvalene. (4)
- 28a. Explain the photoreduction of benzophenone using 2-propanol. What is the quantum yield of this reaction? (5)
 - b. Explain the Barton reaction in aliphatic compounds with an example. (5)
