# LOYOLA COLLEGE (AUTONOMOUS), CHENNAI – 600 034



### M.Sc. DEGREE EXAMINATION - CHEMISTRY

#### FOURTH SEMESTER - APRIL 2022

### PCH 4501 - ORGANIC SYNTHESIS AND PHOTOCHEMISTRY

Date: 15-06-2022	Dept. No.	Max.: 100 Marks

Time: 01:00 PM - 04:00 PM

### **PART-A**

## **Answer ALL Questions.**

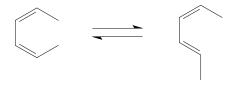
 $(10 \times 2 = 20)$ 

- 1. Mention any two advantages of LDA over n-butyllithium.
- 2. Identify the intermediate and the product in the following reaction.

3. Predict the products in the following conversions.

HO 
$$R^{\frac{1}{2}}$$
 periodic acid ?

- 4. What is the product formed when quinhydrol is electrochemically oxidised?
- 5. What is functional group addition? How is it performed during a real synthesis? Give an example.
- 6. What type of synthons are used during 1,2-diffunctional compound synthesis? Give an example.
- 7. What are the salient features of pericyclic reactions?
- 8. Effect the following conversion.



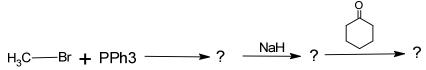
- 9. What is Leukart reduction? Give an example.
- 10. Differentiate between photophysical and photochemical processes.

### PART – B

### Answer any EIGHT Questions.

 $(8 \times 5 = 40)$ 

- 11. Draw the structure of 18-Crown-6 and explain its synthetic applications.
- 12. Complete the following scheme and justify with suitable mechanism.



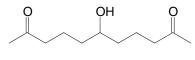
- 13. Outline the mechanism of Sharpless asymmetric epoxidation.
- 14. Predict the products in the following electrochemical reactions.
- (a) Electro-reduction of (i) benzyl bromide and (ii) CH<sub>3</sub>
  Br

- (b) Electro-oxidation of Ph<sub>2</sub>CHCH<sub>2</sub>COO<sup>-</sup>
- 15. Identify the suitable reagents for the following conversions.

$$H_3C$$
 $O$ 
 $CH_3$ 
 $O$ 
 $CH_3$ 
 $O$ 
 $CH_3$ 

$$H_3C$$
  $CH_3$   $?$   $H_3C$   $H$ 

- 16. Draw the correlation diagram for the electrocyclization of 1,3-butadiene involving *con*-rotation. Predict whether the reaction is thermally or photochemically allowed.
- 17. How is degenerate sigmatropic rearrangement explained in bullvalene? Draw at least 4 rearranged structures.
- 18. FGI is a more beneficial retrosynthetic conversion. Justify it with suitable examples.
- 19. Explain the retrosynthetic analysis of the following compounds.
- (a) (b) O OMe



- 20. How are protecting groups helpful to overcome chemoselectivity in reactions? Explain them with any two examples.
- 21. Analyse the photophysical processes with the neat sketch of Jablonski Diagram.
- 22. Write a note on the photoreduction reactions.

### PART - C

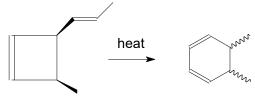
### Answer any FOUR Questions.

 $(4 \times 10 = 40)$ 

- (a) Investigate the mechanism of Ziegler-Natta catalyst in stereoregular polymerization process.
- (b) Delineate the application of silane reagents as protecting groups. (4)
- 24 (a) Compare the Heck and Sonogashira coupling reactions. (6)
- (b) Formulate a mechanism to find out the product. (4)

- 25 (a) How is nitrobenzene electrochemically reduced under (i) strongly acidic and (ii) weakly acidic conditions. (3+3)
- (b) Write the mechanism of the following reaction and predict the stereochemistry of the product.

  (4)



- 26 (a) Give an example for [9,9]-sigmatropic rearrangement and write the mechanism of the reaction. (5)
- (b) Why is stepwise synthesis less yielding than convergent synthesis? Give suitable reasons. (5)
- 27 (a) How are C-C disconnections carried out systematically? Explain any two methods in detail. (5)
- (b) Explain any one method each of 1,2- and 1,3-difunctional compound synthesis. (5)
- 28. Account for the following conversions. (3+3+4)

(ii)
$$hv \longrightarrow O \longrightarrow CH_3$$

$$CH_3 \longrightarrow CH_3$$

$$CH_3 \longrightarrow CH_3$$

$$CH_3 \longrightarrow CH_3$$

$$Major \longrightarrow Minor$$

$$H_3C \longrightarrow OH \longrightarrow H$$

$$H \longrightarrow O \longrightarrow CH_3$$

$$CH_3 \longrightarrow CH_3$$

$$H \longrightarrow CH$$