## LOYOLA COLLEGE (AUTONOMOUS), CHENNAI – 600 034

# M.Sc. DEGREE EXAMINATION – CHEMISTRY

#### FOURTH SEMESTER - APRIL 2024

#### PCH4MC01 - ORGANIC SYNTHESIS AND PHOTOCHEMISTRY

	Date: 01-04-2024 Dept. No. Max. : 100 M Time: 01:00 PM - 04:00 PM	ark
SECTION A – K1 (CO1)		
	Answer ALL the questions $(5 \times 1 = 5)$	)
1	Fill in the blanks	
a)	The by product in meta-chloroperbenzoic acid based oxidation is	
b)	Ugi reaction is a reaction.	
c)	An example for cationic synthon is  The FMO picture of HOMO* of 1,3,5-hexatriene is .	
d)	The FMO picture of HOMO* of 1,3,5-hexatriene is	
e)	For benzophenone, the population of excited state electron in the triplet state is%.	
SECTION A – K2 (CO1)		
	Answer ALL the questions (5 x 1 = 5	5)
2	Answer the following	
a)	Mention an example for a stabilized radical with structure.	
b)	Predict the reagent used for the given deprotection.	
	→ H <sub>2</sub> N OH	
c)	What is functional group addition? Give an example.	
d)	State Woodward Hoffmann rules for cycloaddition reactions.	
e)	What are photosensitizers? Mention their importance.	
SECTION B – K3 (CO2)		
	Answer any THREE of the following $(3 \times 10 = 3 \times 10)$	<del>(0)</del>
3	(a) How would you convert pyruvic acid into amino acid, alanine? Explain the uniqueness of the	
	reagent. (5+5	5)
	Pyruvic acid $\stackrel{NH_2}{\longrightarrow}$ ? $\stackrel{NH_2}{\longrightarrow}$ Alanine	
	(b) Demonstrate the utilities of AIBN and n-Bu <sub>3</sub> SnH in organic synthesis.	

Compare the mechanism and application of Stille and Negishi coupling in C-C bond formation. (a) How are 1,3-difunctional compounds synthesized? (5+5)(b) Explain the stereoselective reactions. How are they useful in organic synthesis? (a) What are the various types of electrocyclization reactions? Explain each one with an example. 6 (6+4)(b) Discuss [1,5]-sigmatropic rearrangement reactions. Write its mechanism and predict whether the geometry of the final product is retained or inverted. (a) Predict the products in the following photochemical reactions. ((3+3)+4)C<sub>6</sub>H<sub>5</sub>COC<sub>6</sub>H<sub>5</sub> hv HOOC COOH + CH<sub>3</sub>CH(OH)CH<sub>3</sub> ii) (b) Write the mechanism of Barton reaction in steroids. SECTION C – K4 (CO3)  $(2 \times 12.5 = 25)$ Answer any TWO of the following 8 (a) Propose a methodology to convert trans-3-hydroxy prolineone of the major amino acid present in collagen into cis-3-hydroxy proline. Explain with mechanism. (7.5+5)(b) Outline the application of copper acetyl acetonate in C-C and C-O bond formation reactions. 9 (a) Appraise the advantages of click chemistry in synthesizing diverse organic compounds. (6.5+6) (b) Predict the product and investigate the mechanism of the following reaction. (a) Discuss any four methods of C-C disconnection approaches with suitable example. (6.5+6)10 (b) What are protecting groups? How are amine and alcohol protected and deprotected? (a) Draw correlation diagram for the cycloaddition reaction of two ethylene molecules. State whether the reaction takes place by thermal or photochemical conditions. (6.5+6)(b) Draw Jablonskii diagram and discuss the kinetics of photophysical processes. **SECTION D – K5 (CO4)** Answer any ONE of the following  $(1 \times 15 = 15)$ (a) Formulate the significance of electroreduction reactions in molecular syntheses. (6+4+5)(b) Show that Tischenko reaction is a disproportionation reaction with example.

(c) Predict the product and explain the mechanism of reaction.

- (a) How is functional group interconversion helpful to synthesize the target molecules effectively with less or no byproducts? Explain with any two examples. (5+5+5)
  - (b) Explain the mechanism of the following reaction and predict the stereochemistry of the mentioned H atoms in the product.

(c) Discuss the photochemistry of  $\alpha,\beta$ -unsaturated ketones in polar and nonpolar solvents.

### SECTION E – K6 (CO5)

#### Answer any ONE of the following

 $(1 \times 20 = 20)$ 

((5+5)+5+5)

14 (a) Identify the products and Rationalise with mechanism.

(b) Design a synthetic scheme for the following compound based on Ullmann coupling and Justify with mechanism.

- (c) Compare Sakurai and Brook rearrangement reactions.
- (a) Perform retrosynthetic analysis of the following compounds and predict a suitable synthetic pathway. (8+6+6)

(b) Predict the mechanism of the following reactions.

(c) Derive Stern Volmer expression.

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