# STELLA MARIS COLLEGE (AUTONOMOUS) CHENNAI-86 (For candidates admitted from the academic year 2019-20 & thereafter)

**SUBJECT CODE: 19CH/PC/OC24** 

## M. Sc. DEGREE EXAMINATION, APRIL 2023 BRANCH IV- CHEMISTRY SECOND SEMESTER

PA	OURSE : CORE .PER : ORGAN ME : 3 HOUR		Y – II CTION – A	MAX. MARKS: 100			
	swer all the questions Choose the correct a	•		$(20 \times 1 = 20)$			
1.	a) 2-bromo-2-methylb	the following alkyl halide will form tertiary alcohol on reaction with H <sub>2</sub> O/H <sup>+</sup> ? to-2-methylbutane b) 2-bromo-3-methylbutane ethyl-1-bromopropane d) all of these					
2.	The condensation of acetaldehyde with HCHO in the presence of NaOMe forms  a) 3-hydroxypropanal b) 3-hydroxypropanal c) Ethanoic acid & Methanol c) Ethanol & formic acid						
3.	In the reduction reactive reagent forms a) cis-4-t-butyleycloho c) Both (a) & (b)	as the	major product.				
4.	The photolysis of 2-he a) Propene + propanoi c) ethene + butanoic a	ne	b) Ethene + 2-butanon d) cyclohexanone	) Ethene + 2-butanone			
5.	Conversion of 3-phenis an example of b)	rearra	angement.	ene under thermal condition d) None of these			
II	Fill in the blanks:						
6.	The key intermediate formed in the Hofmann rearrangement is						
7.	The product formed in the amination reaction of pyridine is						
8.	(COCl) <sub>2</sub> in DMSO is called as						
9.	The photolysis of an alkyl nitrite to form a $\delta$ -nitroso alcohol is reaction.						
10.	The product formed be	etween the reaction	on of cyclopentadiene an	nd <i>p</i> -benzoquinone is			

#### **III** State whether true or false:

- 11. Ylides derivatives are carbon nucleophiles.
- 12. Hydroboration of propene follows anti Markovnikovs' addition.
- 13. LDA is a non-nucleophilic base.
- 14. Photo oxidation of olefin forms peroxide derivatives as major product.

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15. Oxy-Cope rearrangement is an example of sigmatropic reaction.

#### IV Answer in a line or two:

- 16. Why are carbene additions to olefin non-stereospecific in gas phase?
- 17. Mention the key intermediate formed in the Fries rearrangement.
- 18. What is Jones reagent?
- 19. Write the Woodward Hoffmann rules for electrocyclization reaction.
- 20. Give an example for chelotropic reaction.

## SECTION - B

## **ANSWER ANY FIVE QUESTIONS:**

(5x8=40)

(3)

21. Predict the product and justify you answer with suitable mechanism. (4 +4)

(i) 
$$\underbrace{\frac{\text{Zn}/\text{BrCH}_2\text{COOC}_2\text{H}_5}{\text{Zn}/\text{BrCH}_2\text{COOC}_2\text{H}_5}}_{\text{Product}} \xrightarrow{\text{H}^+/\text{H}_2\text{O}} \text{Product}$$
 (ii)  $C_6\text{H}_5\text{COC}_6\text{H}_5 \xrightarrow{\text{H}_2\text{NOH}} \xrightarrow{\text{H}^+} \xrightarrow{\text{H}_2\text{O}} \text{Product}$ 

- 22. a) Apply neighbouring group participation principle and identify the product. (4)
  - HO  $NH_2$   $\frac{NaNO_2/HCl}{0-5 °C} \longrightarrow Produc$
  - b) Write the coupling reaction of benzophenone in presence of TiCl<sub>4</sub> / Zn(Cu). (4)
- 23. a) Explain Shapiro reaction using suitable example. (5)
  - b) Mention the role of KOH in the Reimer-Tiemann reaction. (3)
- 24. How are *cis* and *trans* diols synthesised from olefins by Woodward and Prevost Hydroxylation methods? (8)
- 25. a) Effect the following conversion with suitable mechanism. (5)

$$\begin{array}{c}
\text{OH} \\
\text{Ph} \\
\text{Ph}
\end{array}$$

- b) What is Norrish type II reaction?
- 26. Explain the following with suitable examples. (4+4)
  - a) Paterno-Buchi reaction of alkenes b) Claisen rearrangement ...3

27. Draw correlation diagram for the cycloaddition of 1,3-butadiene and ethylene. Predict whether the reaction is thermally or photochemically allowed.

### SECTION - C

## **ANSWER ANY TWO QUESTIONS:**

(2x20=40)

- 28. a) Explain acyloin condensation reaction with suitable mechanism. (6)
  - b) Predict the product for the reaction of benzamide with Br<sub>2</sub>/ NaOH. (5)
  - c) Suggest suitable mechanism for the following conversion. (5)

$$\begin{array}{c} O \\ + HN_3 & \xrightarrow{H_2SO_4} \\ \hline \\ NH & O \end{array}$$

- d) Give the reaction of ethylacetate with 2 moles of methylmagnesium bromide. (4)
- 29. a) Predict the product and justify your answers with suitable mechanism. (5+5)

(i) O 1. Pyrrolidine 
$$2. CH_2=CHCOCH_3$$
 ? (ii)  $CH_3COCH_3$  +  $COOEt$   $COOET$ 

- b) Explain the reaction between anisole and Birch reagent with suitable mechanism. (5)
- c) Identify **A**, **B** & **C**. (2 + 2 + 1)

$$\begin{array}{c|c}
OH & 1. DMSO, COCl_2 \\
\hline
2. Et_3N
\end{array}
\xrightarrow{PhCO_3H} 
\xrightarrow{B} 
\begin{array}{c}
H^+ \\
\hline
H_2O
\end{array}
\xrightarrow{C}$$

- 30. a) Explain Barton reaction mechanism with suitable example. (6)
  - b) Give an example for [1,3] and [1,5]-sigmatropic rearrangement reactions. Predict the stereochemistry of their final products with the help of FMO diagrams. (8)
  - c) Explain Cope rearrangement using divinylcyclopropane as substrate. (6)

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