CHEM/VI/CC/18

Student's Copy

2024

(CBCS)

(6th Semester)

CHEMISTRY

TENTH PAPER

(Organic Chemistry-III)

Full Marks : 75

Time : 3 hours

The figures in the margin indicate full marks for the questions

(SECTION : A-OBJECTIVE)

(Marks: 10)

Tick (✓) the correct answer in the brackets provided :

 $1 \times 10 = 10$

- β-bond cleavage is observed in which of the following photochemical processes?
 - (a) Norrish type–I ()
 - (b) Norrish type-II ()
 - (c) Paterno-Buchi reaction ()
 - (d) All of the above ()

2. The energy required for various electronic transitions is in the order of

$$\begin{array}{ll} (a) & \sigma \to \sigma^* > n \to \sigma^* > \pi \to \pi^* > n \to \pi^* & (&) \\ (b) & \sigma \to \sigma^* > n \to \sigma^* > n \to \pi^* > \pi \to \pi^* & (&) \\ (c) & \sigma \to \sigma^* > n \to \pi^* > n \to \sigma^* > \pi \to \pi^* & (&) \\ (d) & \sigma \to \sigma^* > \pi \to \pi^* > n \to \pi^* > n \to \sigma^* & (&) \end{array}$$

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| Contd.

- 3. The ground state LUMO of 1,3,5,7-octatetraene has
 - (a) C_2 -symmetry and 3 nodes ()
 - (b) m-symmetry and 4 nodes ()
 - (c) C_2 -symmetry and 4 nodes ()
 - (d) *m*-symmetry and 3 nodes ()
- According to Woodward-Hoffmann rule, a cycloaddition reaction is photochemically allowed
 - (a) when the total number of $(4q+2)_s$ and $(4r)_a$ components is odd ()
 - (b) when the total number of $(4q+2)_s$ and $(4r)_a$ components is even ()
 - (c) when the total number of $(4q+2)_a$ and $(4r)_s$ components is odd ()
 - (d) when the total number of $(4q+2)_{\alpha}$ and $(4r)_{s}$ components is even ()
- Propan-2-one on treatment with alkyl magnesium bromide followed by hydrolysis yields
 - (a) primary alcohol ()
 - (b) secondary alcohol ()
 - (c) tertiary alcohol ()
 - (d) None of the above ()
- 6. The product obtained from the following reaction

$$\begin{array}{c} \overset{O}{\downarrow}_{Cl} + & \swarrow_{Zn} & \longrightarrow ? \\ \end{array}$$

is

- (a) alcohol (
- *(b)* ester ()
- (c) aldehyde ()
- (d) ketone ()

- 7. In Wittig reaction, a phase transfer catalyst alkyltriphenylphosphonium salt reacts with sodium hydroxide to generate ylides, which combines with aldehydes to produce
 - (a) alkanes ()
 - (b) alkenes ()
 - (c) alkynes ()
 - (d) cycloalkanes ()
- 8. Consider the following statements and select the correct answer :
 - Microbial oxidation occurs under mild condition and in dilute solution.
 - (ii) Baker's yeast can act as reducing agent and it selectively reduces b-ketoesters and b-diketones.
 - (a) Only (i) is true ()
 - (b) Only (ii) is true ()
 - (c) Both (i) and (ii) are true ()
 - (d) Both (i) and (ii) are false ()
- 9. The number of NMR signals present in 1,1,2-tribromoethane is
 - (a) 1 ()
 - (b) 2 ()
 - (c) 3 ()
 - (d) 4 ()
- 10. The distance between the centres of the two adjacent peaks in a multiplet is called
 - (a) base peak ()
 - (b) molecular ion peak ()
 - (c) chemical shift ()
 - (d) coupling constant ()

(SECTION : B-SHORT ANSWERS)

(Marks: 15)

Answer the following questions :

Unit—I

1. State Franck-Condon principle and explain.

OR

2. Explain singlet and triplet states of an electron.

Unit—II

 Explain suprafacial and antarafacial orbital overlap of cycloaddition reaction.

OR

4. "The $[\pi_s^2 + \pi_s^2]$ cycloaddition reaction is photochemically allowed but thermally forbidden." Explain.

UNIT—III

5. Mention one method of preparation of sulphonamides. What happens when sulphonamides are heated with aqueous acids? Give example.

OR

6. Complete the following reaction with suitable mechanism :

$$(CH_3)_2 CHLi + CO_2 \longrightarrow ? \xrightarrow{Hydrolysis} \Delta$$

Unit—IV

7. Complete the following reaction with suitable mechanism :

$$H_{2O} + H_{Me} + (HCHO)_3 \xrightarrow{H_2O} ?$$

3×5=15

8. Green chemistry is important in alternate reaction pathways. Explain with aldol reaction.

Unit—V

9. How will you distinguish between CH₃CH₂Cl and CH₃CH₂OH in NMR spectroscopy?

OR

10. In a normal mass spectrophotometer, 2-hexanol shows the following fragmentation pattern :

m/z = 45, 59, 73, 84, 87, 102

Showing the entire fragmentation pattern, determine the structures of the above fragments.

(SECTION : C-DESCRIPTIVE)

Answer the following :

Unit—I

1. (a) Draw the Jablonski diagram and explain the following : 2+5=7

- (i) Vibrational relaxation
- (ii) Internal conversion
- (iii) Intersystem crossing
- (iv) Fluorescence
- (v) Phosphorescence

(b) Explain the following :

Quantum yield, Quenching and Photosensitization

OR

2. (a) "Irradiation of benzophenone solution in 2-propanol with light of 345 nm causes benzophenone to undergo $n \rightarrow \pi^*$ transition followed by hydrogen abstraction from 2-propanol to form benzopinacol." Write the chemical reactions involved.

5

10×5=50

9 Write the products of the following reaction :

$CH_3COCH_2(CH_2)_2CH_3 \xrightarrow{hv} ?$

<u>0</u> What is Paterno-Buchi reaction? Explain with suitable examples.

1.0

UNIT-II

- ω <u>a</u> What are modes of electrocyclic reactions? Explain. electrocyclic reactions? What are the two stereochemical
- 6 Based electrocyclic reactions with proper stereochemistry : on FMO approach, predict the products of, the following 3×2=6





(c) What are dienophiles?

OR

- 4 a Based interconversion of cyclohexadiene to on Woodward-Hoffmann rule, 1,3,5-hexatriene system. explain the electrocyclic
- 6 "The photochemically forbidden." Explain. $[\pi_{s}^{4} + \pi_{s}^{2}]$ cycloaddition reaction is thermally allowed but
- <u>c</u> Predict the products of the following with proper stereochemistry

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11/2×2=3

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UNIT-

(a) Complete the following reactions (mechanism not required) : $1 \times 3 = 3$

(i)
$$CH_3CH_2Br + KSH \longrightarrow ?$$

(ii)
$$CH_3Br + C_2H_5SNa \longrightarrow ?$$

(iii)
$$\bigvee F + C_6 H_5 Li \longrightarrow ?$$

- 6 Show the guanidine starting from p-acetamidobenzenesulphonyl chloride. What is its main application? 3+step-by-step mechanism for the formation of sulpha-3+1=4
- <u>c</u> Write down one method of preparation of Grignard reagent. happens when Grignard reagent is treated with aldehydes? What 2+1=3

OR

..... (a) Complete the following reactions with suitable mechanisms : (i) CH₃MgBr + CH₃CN -↓ ~ 4+3=7

(ii)
$$(1)^{\text{CHO}} + 2C_2H_5\text{SH} \xrightarrow{\text{HCl}} ?$$

Θ Complete the following reactions (mechanism not required) : 1×3=3

(i)
$$(i)$$
 (i) (i)

(iii)
$$C_6H_5MgBr + H_2C_CH_2 \longrightarrow ?$$

(ii)
$$C_2H_5Li + C_6H_5CH_2Br \longrightarrow ?$$

UNIT-IV

- 7 a) Discuss in brief the method of preparation for aryl vinyl ketones aqueous medium following Hoffmann elimination reaction pathway. 5
- Θ Complete the following reaction with suitable mechanism :

4 ω

$$O_2N \longrightarrow C \longrightarrow CH_3COOOH, H_2SO_4$$
?

<u></u> Explain in detail the process of microbial biochemical reduction with suitable example.

OR

œ (a) Complete the following reactions with suitable mechanisms :

Δ

ω

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$$+ Ph_3 \stackrel{\text{@}}{\to} CH_2 CH_3 \stackrel{\text{Cl}}{\to} \frac{N_3 OH}{CH_2 Cl_3} ?$$

9 Discuss the preparation of 2-chloro-N-aryl anthranilic acid

ω

0 Write a brief note on the application of microbial (enzymatic) oxidation for the preparation of acetic acid and ethyl alcohol. ω

UNIT-V

10 9 a) 9 (a) (c) 6 What is chemical shift in NMR spectroscopy? Discuss the factors that Sketch the H-NMR signal for acetophenone cyclohexane from its molecular ion peak What is affect chemical shift in an NMR spectrum. When 2-methylpentane is bombarded with high energy electron, it got Discuss the basic principles of NMR spectroscopy. fragmented molecular ion peak? Predict all the fragmentation pattern of and gave m/z values at 86, 71, 57 and 43. Determine the OR 1+3=4N 4

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<u></u> Write a brief note on the basic principle of mass spectroscopy. fragmented structures ω ω

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- (c) Paterno-Buchi reaction
- a All of the above ~
- Ņ The energy required for various electronic transitions is in the order of
- (a) 6 a → a. $\sigma \rightarrow \sigma^* > n \rightarrow \sigma^*$ ٧ $n \rightarrow \sigma^*$ $>\pi \rightarrow \pi^* > \pi \rightarrow \pi^*$ > n → π* >π → π*
- (c) a ↓ a V $n \rightarrow \pi^*$ $> n \rightarrow \sigma^*$ > ≒ → ≒*
- (d a ↓ a v z → **π*** $> n \rightarrow \pi^*$ $> n \rightarrow \sigma^*$

- The ground state LUMO of 1,3,5,7-octatetraene has e,
- C₂-symmetry and 3 nodes ø
- m-symmetry and 4 nodes 9
- C2-symmetry and 4 nodes (c)
- m-symmetry and 3 nodes (q)
- is. cycloaddition reaction According to Woodward-Hoffmann rule, a photochemically allowed 4
- 3 is. components $(4r)_a$ of $(4q+2)_s$ and number total the when ppo ø
- components $(4r)_a$ and number of $(4q + 2)_s$ total the when even (q
- 2 components $(4r)_{S}$ and number of $(4q + 2)_a$ total the when ppo ٢
- 12 components (4r)_s number of $(4q+2)_a$ and total the when even (d)
- ą Propan-2-one on treatment with alkyl magnesium bromide followed hydrolysis yields ıю.
- primary alcohol (a)
- secondary alcohol (q)
 - tertiary alcohol
 - 3
- None of the above (q)
- The product obtained from the following reaction ø.

c. + \overline{O}

is.

alcohol ester (a) (q)

aldehyde Ú

ketone (q)

- 7. In Wittig reaction, a phase transfer catalyst alkyltriphenylphosphonium salt reacts with sodium hydroxide to generate ylides, which combines with aldehydes to produce
- alkanes (q) ø
 - alkenes
- alkynes 3
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- Baker's yeast can act as reducing agent and it selectively reduces b-ketoesters and b-diketones. Ξ
- Only (i) is true ø
- Only (ii) is true (q)
- Both (i) and (ii) are true <u>ن</u>
- Both (i) and (ii) are false (q)
- The number of NMR signals present in 1,1,2-tribromoethane is ō.
- ø 9 3
- (q)
- The distance between the centres of the two adjacent peaks in a multiplet is called 10
- base peak ø
- molecular ion peak (q)
- chemical shift 0
- coupling constant (q)

(SECTION : B-SHORT ANSWERS

(Marks: 15)

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UNIT-I

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UNIT--II

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OR

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UNIT-III

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 $(CH_3)_2 CHLi + CO_2 \longrightarrow 2 \xrightarrow{Hydrolysis} 2$

UNIT-IV

Complete the following reaction with suitable mechanism : 2



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In the followin otosensitization 1 in 2-propan go $n \rightarrow \pi^*$ trans

[Contd.

ю

Write the products of the following reaction : a)

∩. ↑ 2 CH₃COCH₂(CH₂)₂CH₃

+

0

What is Paterno-Buchi reaction? Explain with suitable examples. 3

UNIT-II

What are electrocyclic reactions? What are the two stereochemical modes of electrocyclic reactions? Explain. 3. (a)

e

3×2=6 FMO approach, predict the products of the following electrocyclic reactions with proper stereochemistry : uo Based e)





What are dienophiles? (c)

g

- 4 electrocyclic interconversion of cyclohexadiene to 1,3,5-hexatriene system. the explain rule, Woodward-Hoffmann uo Based (a) 4
 - 3 but allowed cycloaddition reaction is thermally photochemically forbidden." Explain. "The $[\pi_{s}^{4} + \pi_{s}^{2}]$ (q)
- <u>(</u>)



UNIT--III

 $1 \times 3 = 3$ •• Complete the following reactions (mechanism not required) 5. (a)

- (i) CH₃CH₂Br + KSH → 2
- (ii) $CH_3Br + C_2H_5SNa \longrightarrow 2$

(iii) $\langle - \rangle - F + C_6 H_5 L_1 \longrightarrow P$

- 3+1=4guanidine starting from *p*-acetamidobenzenesulphonyl chloride. What the formation of sulphastep-by-step mechanism for is its main application? the Show (q)
- 2+1=3What Write down one method of preparation of Grignard reagent. happens when Grignard reagent is treated with aldehydes? 3

OR

- 4+3=7 Complete the following reactions with suitable mechanisms : 6. (a)
- (i) CH₃MgBr + CH₃CN → ?



(ii)
$$(ii)$$
 + $2C_2H_5SH \xrightarrow{HCI}$?

 $1 \times 3 = 3$ Complete the following reactions (mechanism not required) : (q)

(i)
$$\left(\bigcup_{i=1}^{N} - C_{i} + NH(CH_{3})_{2} \xrightarrow{NaOH} \right)^{2}$$

(ii) $C_2H_5Li + C_6H_5CH_2Br \longrightarrow ?$

(iii)
$$C_6H_5MgBr + H_2C-CH_2 \longrightarrow 2$$

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Contd.

		UNITIV	
	7. 6	 Discuss in brief the method of preparation for aryl vinyl ketones in aqueous medium following Hoffmann elimination reaction pathway. 	3
	U) Complete the following reaction with suitable mechanism :	4
		$O_2 N - O_2 N - O_2 N - O_3 COOH P_3 COOH, H_2 SO_4$	
	0	Explain in detail the process of microbial biochemical reduction with suitable example.	3
		OR	
80	s. (a	Complete the following reactions with suitable mechanisms :	4
		$ + Ph_3^{\oplus}CH_2CH_3^{\oplus}CI \xrightarrow{OH}_{CH_2^{\oplus}CI_2^{\oplus}} 2 $	
	(q)	Discuss the preparation of 2-chloro-N-aryl anthranilic acid.	3
	(c)	Write a brief note on the application of microbial (enzymatic) oxidation for the preparation of acetic acid and ethyl alcohol.	m
		UNITV	
6	(a)	What is chemical shift in NMR spectroscopy? Discuss the factors that affect chemical shift in an NMR spectrum.	
	(q)	What is molecular ion peak? Predict all the fragmentation pattern of	
	2	cyclohexane from its molecular ion peak.	
	(c)	Sketch the H-NMR signal for acetophenone.	
		OR	
10.	(a)	Discuss the basic principles of NMR spectroscopy.	
	(q)	When 2-methylpentane is bombarded with high energy electron, it got fragmented and gave m/z values at 86, 71, 57 and 43. Determine the	
		fragmented structures.	
	(c)	Write a brief note on the basic principle of mass spectroscopy. 3	

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