REV-00 MSC/94/104



M.Sc. CHEMISTRY First Semester ORGANIC CHEMISTRY-I (MSC - 101)

Duration: 3Hrs.

Full Marks: 70

Part-A (Objective) =20 Part-B (Descriptive) =50

(PART-B: Descriptive)

Duration: 2 hrs. 40 mins.

Marks: 50

Answer any *five* of the following questions:

- (a) (i) SN¹ reaction don't proceed at bridgehead carbon in [2,2,1] bicyclic compound. However, for those SE¹ is quite possible. Explain why?
 (2,5+2,5=5)
 - (ii)Write the product of the following reaction along with suitable mechanism.

 $Et \longrightarrow P_2O \longrightarrow ?$

(b) (i) Explain the following observation and also mention the type of mechanism involved in the following reaction. (3+2=5)



(ii) Write the product of the following reaction with mechanism-

2. (a) (i) Predict the direction of the following reaction using HSAB principle- (2)

 $\int_{-\infty}^{0} + RO^{*} \longrightarrow \int_{-\infty}^{0} + RS^{*}$

HCI ?

- (ii) The ratio of K_{H}/K_{D} for the following reaction is 7. On the basis of this propose a mechanism for the reaction. (3) $CH_{3}COCH_{3} + Br_{2} \longrightarrow CH_{2}(Br)COCH_{3} + HBr$
 - $CH_3COCD_3 + Br_2 \longrightarrow CD_2(Br)COCD_3 + DBr$
- (b) Write down Hammett equation and explain each term used in the equation.Why Hammett equation is called as linear free energy relationship? (3+2=5)
- 3. (a) Why Hammett plots gives almost straight line for para, meta and unsubstituted benzene derivatives? However, for aliphatic and o-substituted compounds deviation from linearity is observed?
 - (b) (i) Arrange the following acid in order of their increasing strength-CH₃COOH, ClCH₂COOH, FCH₂COOH, ICH₂COOH
 - (ii) Basicity for methyl amine is more than that of ammonia while basicity of aniline is less than that of methyl amine. Explain why?
- 4. (a) Explain with example, what do you mean by an ambident nucleophile? (2)
 - (b) Give the products of the following reaction that favours SN² and that favours SN¹ mechanism.
 (3)

Br CH₃O⁻ ?

- (c) Discuss in details how the following factors affect an SN¹ reaction?
 - (i) Structure of the substrate.
 - (iii) Nature of solvent
- 5. (a) Using the required substrate and the nucleophile, prepare the following compounds.

(i) CH₃-CH₂-CH₂-OCH₃

(ii) CH₃-CH₂-CH₂-CH₂-SCH₃

(ii) Nature of nucleophile

(5)

(2)

(3)

- (b) Give the product of the following reactions with mechanism.
 - (i) $(i) \xrightarrow{\text{NaNH}_2 / \text{NH}_3 (I)}_{\text{CI}} ?$ (ii) $(ii) \xrightarrow{\text{CI}}_{\text{CI}} ?$

(c) Write down the product with stereo-chemistry of the following reactions with mechanism. (2+3=5)

$$HOOC \xrightarrow{H_{H}} Br \xrightarrow{CH_{3}O} ?$$

	H Contraction of the second		
6.	(a) Why aniline doesn't undergo Friedel Craft alkylation?	(2)	
	(b) What is o/p ratio? How steric factors affect the o/p ratio?	(3)	
	(c) Write about arenium ion mechanism giving energy profile diagram.	(5)	
7.	7. (a) Write about Wittig Rearrangement.		
(b) Complete the following reaction with mechanism.		(3)	
	O Conc. H ₂ SO ₄		

$$\begin{array}{c} O \\ H_{2} \\ O \\ H_{3} \end{array} \xrightarrow{\text{Conc. } H_{2} \\ S \\ H_{3} \\ H_{3} \\ \end{array}$$

- (c) Write short notes on following: $(2.5 \times 2=5)$
 - (i) Sommelet Hauser Rearrangement
 - (ii) Favorskii Rearrangement
 - 8. (a) Write the product of the following:

 $(1 \times 2 = 2)$



- (b) Write short notes on Pinacol Pinacolone Rearrangement.
- (c) Complete the following with mechanism:

 $(2.5 \times 2 = 5)$

(3)



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PART-A (Objective)

(III) CI (IV) CI

Duration: 20 minutes

Time: 20 mins

I. Choose the correct option:

1. Which pair will not form a stable carbocation?

(II)

- (I) Cl
- (a) I and II

(a)

2. Which of the following reaction gives carbene as intermediate?

(b) II and III

(I)
$$CH_2N_2 \xrightarrow{\text{Light}}$$
 (II) $\stackrel{R}{\longrightarrow} C=0 \xrightarrow{\text{Light}}$
(III) $RCON_3 \xrightarrow{\text{Light}}$ (IV) $\underset{R}{\longrightarrow} N=C=0 \xrightarrow{\text{Light}}$
(a) I and II (b) I, II and III (c) III and IV

3. The following reaction is an example of -

4. Which of the following reaction don't involve carbocation?
(a) (CH₃)₃CCl + AgNO₃ ______
(b) (CH₃) COL + UCl

(c)

(d)

(b) $(CH_3)_3COH + HC1 \longrightarrow$ (c) $(CH_3)_3CH + Cl_2 + Light \longrightarrow$

(b)

- (d) $CH_3CH=CHCH_2OH + H_3O^+$
- 5. Which of the following structure is not aromatic?

(c) II and IV

(d) III and IV

(d) I and III

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Marks – 20

Total Marks: 20

1×20=20

6. Which of the following structures are aromatic?

(d) None of these (a)

- 7. In which of the following mechanism carbanion is involved? (a) SN^2 (b) SN^1 (c) SE^2 (d) SE^1
- 8. Which is a correct statement for an SN^2 reaction? (a) Follow 2nd order kinetics.
 - (b) Weak nucleophile will favour the reaction.
 - (c) Carbocation is formed as an intermediate.
 - (d) All these statements are correct.
- 9. Decreasing order of nuceophilicity of (1) CH₃S⁻, (2) CH₃COO⁻, (3) CH₃OH, is (a) 1 > 2 > 3(b) 2 > 3 > 1(c) 3 > 2 > 1 (d) 1 > 3 > 2

10. Which of the following substrate will produce rearranged product under SN¹ condition?

(a) Br (b) Br (c) (d) Br

11. The following substitution reaction

(2S,3R)-2-chloro-3-methylpentane <u>Conc.</u> CH₃O⁻ ? , will produce

(c) (2S,3S)-2-methoxy-3-methylpentane (d) (2S,3R)-2-methoxy-3-methylpentane

(a) (2R,3R)-2-methoxy-3-methylpentane (b) (2R,3S)-2-methoxy-3-methylpentane

12. Which of the following substrate will exhibit neighboring group participation?

(a) \xrightarrow{SMe} (b) \xrightarrow{Ci} (c) \xrightarrow{I} (d) \xrightarrow{I} OH

13.List the following in order of decreasing reactivity towards hydrolysis:

1)CI	2)OEt	3)
(a) $1 > 2 > 3$	(b) $2 > 3 > 1$	

(c) 3 > 2 > 1 (d) 1 > 3 > 2

14. The electrophile involved in sulphonation of aromatic system is (a) SO_3 (b) SO_3H (c) H_2SO_4 (d) None of the above

15. Which of the following rearrangement reaction involves electron rich carbon? (a) Favorskii Rearrangement (b) Pinacol Pinacolone Rearrangement (c) Curtius Rearrangement (d) None of the above

- 16.In Losssen Rearrangement, the eliminating group is (c) HCl (a) –OCOR (b) N_2 (d) None of the above
- 17.In Neber Rearrangement, the intermediate is (b) Carbocation (a) Carbene
 - (c) Azirene (d) None of the above



BnOH₂C

BnOH₂C

 $Bn = C_6H_5CH_2-$

(a) Perbenzoic acid(c) Sulphuric acid

(b) HN₃

(d) None of the above
