

UNIVERSITY OF NORTH BENGAL B.Sc. Honours 2nd Semester Examination, 2023

CC3-CHEMISTRY

ORGANIC CHEMISTRY

NEW AND OLD SYLLABUS

Time Allotted: 2 Hours

The figures in the margin indicate full marks.

GROUP-A

1. Answer any *five* questions from the following:

- (a) Cyclo-octatetraene readily forms potassium salt when it is reacted with potassium. Why?
- (b) Compare the stability of $(NH_2)_2 C = \overset{\oplus}{NH_2}$ and $H_3 \overset{\oplus}{N-C} = NH$.
- (c) Draw the stereochemical structure of (2S, 3R)-Isomer of 3-bromo-2-butanol in sawhorse projection formula.
- (d) Acrylic acid is stronger than propanoic acid. Explain why.
- (e) Trimethyl amine is less basic than dimethyl amine in aqueous medium. Why?
- (f) Explain why HCN does not add to $CH_2 = CH Me$ but adds to $CH_2 = CH COMe$.
- (g) Despite being an alkane, cyclopropane often shows its reactive character. Why?
- (h) Assign R/S designation for following compounds:



GROUP-B

2. Answer any *three* questions from the following:

 $5 \times 3 = 15$

3

(a) (i) pK_a values of maleic acid and fumaric acid vary differently. Suggest proper reasons for this variation.

 $1 \times 5 = 5$

Full Marks: 40

(ii) Between the two carbocations, which is more stable and why?



(b)	(i)	In which compound $C = O$ bond length is longer. Justify your answer.	$2\frac{1}{2}$
		CH ₃ CHO and CF ₃ CHO	2
	(ii)	C–Cl heterolysis of (Me ₃ C) ₃ CCl is faster than that of Me ₃ CCl. Justify.	$2\frac{1}{2}$
(c)	(i)	The direct reaction of an alcohol with NaBr does not give any alkyl bromide but the reaction proceeds well when few drops of conc. H_2SO_4 is added. Explain.	$2\frac{1}{2}$
	(ii)	Justify that NH_2NH_2 is a stronger nucleophile than NH_3 but a weaker base.	$2\frac{1}{2}$
(d)	(i)	When aniline is subjected to Friedel Crafts alkylation in presence of catalytic amount of $AlCl_3$ alkylation does not occur, but with large excess of $AlCl_3$, a very small amount of <i>m</i> -product is obtained. Explain.	$2\frac{1}{2}$
	(ii)	How would you establish that mechanism of ozonolysis, involves the formation of zwitter ion as intermediate?	$2\frac{1}{2}$
(e)	(i)	What are singlet and triplet carbenes? Why triplet carbenes are more stable than singlet carbene?	$2\frac{1}{2}$
	(ii)	Explain that unlike chlorination, iodination of methane is unsuccessful.	$2\frac{1}{2}$

GROUP-C

3.		Answer any <i>two</i> questions from the following:			
	(a)	(i)	Optically active CH ₃ CH(Br)CH(Br)CH ₃ has positive dipole moment	3	
			while the meso form has zero dipole moment. Explain.		
		(ii)	Why are the racemic modifications optically inactive? Discuss with suitable example.	2	
		(iii)	Dissociation of <i>t</i> -BuCl in water requires only 20 kcal.mol ^{-1} of energy but in absence of water it requires 150 kcal.mol ^{-1} . Justify the statement.	2	
		(iv)	Find the stereochemical relationships of the following structures (A to D): COOH H	3	



[Hints: Consider all possible pairs AB, AC, AD, BC, BD and CD]

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(b) (i) Complete the following reactions:

H₃C - C = CH
$$\xrightarrow{\text{HgSO}_4}_{\text{H_2SO}_4, \text{H_2O}}$$
?
 $\overbrace{\text{Et} \text{Cl}}_{\text{Anhy. AlCl}_3}$?
(ii) $\overbrace{\text{O}}_{\text{H}_A}^{\text{HB}}$

How do you classify the two hydrogens marked as H_A and H_B ? Are they prochiral or not?

(iii) Write short notes on:

Electrophilic substitution reaction on aromatic hydrocarbon and Hydroboration-oxidation process in an alkene.

(c) (i) The cyclopropane D loses its proton in hydrogen exchange reactions 10000 times faster than cyclopropene E. Explain.



(ii) Carry out the following transformation with suitable mechanisms:



(iii) Arrange the following compounds in order of increasing pK_a values with reasoning. F_3C CF_3



(iv) Distinguish between 1-butyne and 2-butyne by a chemical test.

(d) (i) Compare the stability of the following:

$$\triangleright_{\Theta}$$
 , \geq_{Θ} , \square_{Θ}

$$Cl \longrightarrow \dot{C}H_2$$
, $Br \longrightarrow \dot{C}H_2$, $I \longrightarrow \dot{C}H_2$

(ii) Draw the resonating structures of the following and indicate the most $1\frac{1}{2}$

$$\ddot{\mathrm{CH}}_2 - \mathrm{CH} = \mathrm{CH} - \mathrm{CH} = \mathrm{O}$$

- (iii) The difference in pK₁ and pK₂ values for dicarboxylic acids of the type $1\frac{1}{2}$ HOOC(CH₂)_n COOH decreases as 'n' increases. Explain.
- (iv) Compare the rate of bromination of nitrobenzene with that of bromobenzene. Also explain the orientation effect in these reactions.

×.

1

3

2 + 2

 $2 \times 2 = 4$

2

4

3

 $2 \times 2 = 4$