RAMAKRISHNA MISSION VIDYAMANDIRA

(Residential Autonomous College affiliated to University of Calcutta)

B.A./B.Sc. SECOND SEMESTER EXAMINATION, JUNE 2022

FIRST YEAR (BATCH 2021-24) **CHEMISTRY (HONOURS)**

Paper: III [CC3] Full Marks: 50 Time: 11.00 am - 1.00 pm

[Use one Answer book for <u>Unit - I & IV</u> and another Answer book for <u>Unit - II & III</u>]

Unit: I

Answer **any one** question:

Date : 20/06/2022

[12 marks]

a) Comment on the enol contents of the following two compounds

[2]

i) CH₃COCOCH₃ and

Arange the following carbocations in increasing order of reactivity and also explain your answer. [2]

- Draw the orbital picture for sight and triplet carbene. Give one example of nucleophilic carbene and why it is called so.
 - When diazoamino benzene boiled with HCl the istopic nitrogen found to be present in both [2]
- aniline and nitrogen explain with mechanism.
 - Draw the energy profile diagram for the following equilibrium:-

$$A \xrightarrow{K_1} B \xrightarrow{K_2} C (K_1 > K_2)$$

which one is the major product after equilibration of the reactions.

[2]

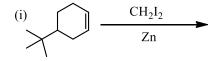
[2]

- Draw the resonance structures of the following intermediates and indicate the most stable resonance hybrid in each case :-
 - [2]

(i)
$$CH_3 - \overset{\oplus}{C} = O$$
 (ii) $CH_3 - CH_3$

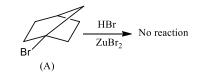
Complete the following reaction with mechanism -

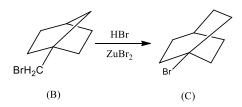
 $[2\times2]$



(ii) $Ph_3COH \xrightarrow{50\% H_2SO_4}$ yellow colour solution Colourless Solution

b) Explain the following observations where substrate 'A' does not react but 'B' gives product - 'C'. [2]

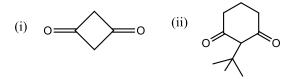




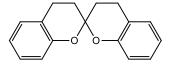
- c) Draw the energy profile diagram for the following reaction for
 - $(i) S_N 1$
 - (ii) $S_N 2$

$$\begin{array}{ccc} \Theta & \text{solvent} & \Theta \\ R\text{-}I\text{+}Nu & & & & \\ \hline & & & \\ \end{array} R\text{-}Nu\text{+}I$$

- (iii) the solvent for the reaction was changed from non-polar to polar. Then what will be change in energy profile diagram.
- d) The following molecules exists in 100% Keto forms. Give suitable reason for the observations. [2]



e) The following molecule is a very good example of thermochromics substance i.e. it is colourless when cold but it is red when sot - explain the observation. [1]



(Thermochromic subsfrance)

Unit: II

Answer **any one** question:

[13 marks]

3. a) Carry out the following conversions. Give mechanism.

 $[2\times2]$

[3]

(i) (R)- 2 - phenylethanol \rightarrow (R) - 2 - phenylethylchloride

$$\stackrel{\text{(i)}}{\bigodot} \longrightarrow \stackrel{\text{OH}}{\bigodot}$$

b) Predict the product(s) of the following reactions and suggest plausible mechanism in each case. $[2\times2]$

(i) (S) - Me (Et) CHOMe
$$\frac{\text{HI}}{\text{Cold condition}}$$

(ii)
$$\frac{H_{\text{MeOH}}}{\text{Me}} \circ \frac{\text{MeOH}}{\text{H}^{\oplus}}$$

c) Explain, showing the stereochemical course of the reaction, what happens when threo - 1- bromo -1,2- diphenylpropane is treated with NaOEt in EtOH. Explain whether, under the same reaction conditions, the erythro isomer will undergo the same reaction at a faster rate or not.

d) Justify or criticise: HO is a better nucleophile than HOO.

 $[2\times2]$

[1]

Predict the product of the following reactions. Give mechanism. 4.

(i)
$$\overset{\circ}{\underset{\circ}{\bigvee}}$$
 $\overset{\circ}{\underset{\circ}{\bigvee}}$ $\overset{\varepsilon}{\underset{\circ}{\bigvee}}$ (ii) $\overset{\varepsilon}{\underset{\circ}{\bigvee}}$

- What happens when $F_3C CHCl_2$ is heated with EtONa in Ethanol? By which path the reaction occurs? Justify.
- [2] Explain the stereochemistry and mechanism of the reaction when threo isomer of
- Ph CH(Me) CH (Me) OTs is treated with acetic acid. [2]
- Cite an example of SN² reaction which is attended by racemisation. [1]
- Me₃C CH₂ Br is inert to SN² reaction, though it is a primary halide. Explain. [2]
- Which one of the following is a better nucleophile? Explain your answer. [2]

PhS or PhO

Unit: III

Answer any one question:

[12 marks]

Complete the following reactions with mechanism.

 $[3\times2]$

[3]

[1]

(i)
$$CH_3$$
- CH = CH - CH_3 (ii) O_3 (ii) $Zn|H_2O$

(ii)
$$OsO_4$$
NMO
acetone /H₂O

- i) Complete the following reactions and also account for the products formation.

 - ii) Justify the following statement: "Hydroboration reaction is more to be Markonifov addition rather than anti-Markonifov addition.
- Describe the preparation and use of $Si\alpha_2BH$. [2]

- Complete the following reactions with mechanism.

 - $NaoH/H_2O_2$

 - Justify the following statement: "Non-polar solvent and high temperature promote allylic bromination reaction when alkene reacts with bromine".
 - Compare the reaction out come between Woodward dihydroxylation and Prevost modification along with mechanism for each. [3]
 - Complete the following reactions (no mechanism required). [1]

Unit: IV

Answer **any one** question: [13 marks] a) Using Chloromethylation reaction, convert benzene into benzyl chloride. Give mechanism.

[2]

 $[3\times2]$

[2]

Both ortho and meta bromoanisole give the same product on treatment with sodamide in liquid ammonia. Write the product with explanation. [2]

Account for the following observations: $[2\times2]$

- (i) Nitration of anisole with N₂O₅ gives mainly ortho nitro product.
- (ii) 1,3 Dichloro 2,5 dinitrobenzene on treatment with methanolic NaOMe produces only 1,3-dichloro - 2- methoxy -5- nitrobenzene.
- Predict the product(s) in the following reactions and explain their formation. $[2\times2]$

(ii)
$$\begin{array}{c} \\ \\ \\ \\ \end{array}$$
 + AlCl₃ + $\begin{array}{c} \\ \\ \end{array}$

Justify or Criticise: Nitration of Cinnamic acid gives predominantly paranitrocinnamic acid. [1] 8. a) Write only the structure of the product formed in the following reactions.

(i)
$$\longrightarrow$$
 AlCl₃ (ii) \longrightarrow Cl \longrightarrow AlCl₃

(iii) OMe OCI
$$\frac{1. \text{ Anh Al Cl}_3 (3\text{eq})}{2) \text{ H}_3 \text{O}^{\frac{1}{4}}}$$
 (iv) $\frac{\text{CN}}{\text{NH}_3}$

b) Discuss the reaction of piperidine with 2,4- dinitrofluorobenzene (DNFB) highlighting SN² (aromatic) mechanism.

 $[4\times1]$

[2]

[2]

[3]

c) Compound (I) on treatment with mixed acid forms only one aromatic product of which the molecular formula is C₈H₈N₂O₅. Account for the reaction.

$$\mathsf{Me} = \underbrace{\mathsf{OMe}}_{\mathsf{OMe}}$$

d) Predict the product(s) of the following reaction and explain their formation.

$$\begin{array}{c}
\text{CI} \\
\hline
\text{KNH}_2
\end{array}$$

$$\begin{array}{c}
\text{NH}_3
\end{array}$$

Cite an evidence in favour of the formation of benzyne intermediate in this reaction.

e) Justify or Criticise: Friedel Craft reaction of benzene with product. [2]

_____x