

Total Pages—15

UG/II/CHEM/H/III/16(Old)

2016

CHEMISTRY

[Honours]

PAPER – III

Full Marks : 90

Time : 4 hours

The figures in the right hand margin indicate marks

Use separate answer scripts for Group A and B

[OLD SYLLABUS]

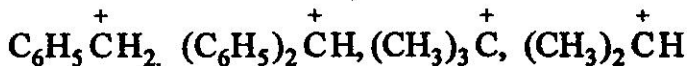
GROUP – A

(Organic)

GROUP – A(a)

Answer any one question : 15 × 1

1. (a) Arrange the carbonium ions in order of increasing stability (least stable first). 2

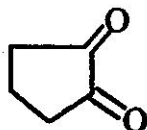
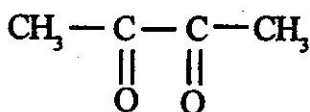


(Turn Over)

(2)

(b) Compare the nucleophilicities and basicities of BuO^- and EtO^- . 2

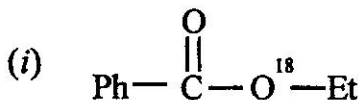
(c) Which one of the following diketones has higher enol-content? Explain. 2



(d) Account for the fact that vinyl chloride does not give a precipitate with alcoholic silver nitrate solution but allyl chloride does. 2

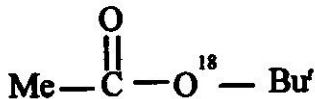
(e) Aldehydes are more reactive than ketones. Justify the statement mentioning two general effects with an example. 3

(f) Give the mechanism of alkaline hydrolysis of the following esters in ordinary water (H_2O^{16}) and indicate the distribution of O^{18} in the products in each case. 2×2



(3)

(ii)



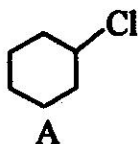
2. (a) Heat of hydrogenation of cyclohexene to cyclohexane is -28.6 Kcal/mole. The observed heat of hydrogenation of benzene to cyclohexane is -49.8 Kcal/mole. Find out the resonance energy of benzene. 3

(b) Distinguish between the molecularity and the order of a reaction. 2

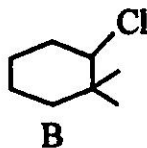
(c) Which substrate in each of the following pair will react more rapidly with hydroxide ion under $\text{S}_{\text{N}}2$ reaction conditions. 2

(i) $\text{p-Br C}_6\text{H}_4\text{CH}_3$ and $\text{C}_6\text{H}_5\text{CH}_2\text{Br}$
A B

(ii)

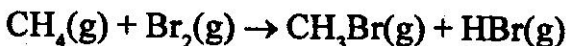


and



- (d) Calculate ΔH° of the reaction and predict whether the reaction will take place or not.

3



Given, $D_{\text{Br}-\text{Br}} = 192.35 \text{ KJ mol}^{-1}$

$$D_{\text{C}-\text{H}} = 414 \text{ KJ mol}^{-1}$$

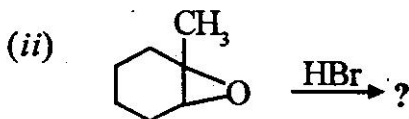
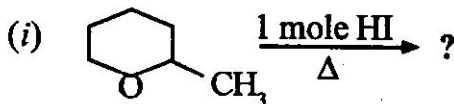
$$D_{\text{C}-\text{Br}} = 276 \text{ KJ mol}^{-1}$$

and $D_{\text{H}-\text{Br}} = 363.8 \text{ KJ mol}^{-1}$

- (e) S_N2 reaction at chiral centre of configuration 'R' always changes its configuration to 'S' and vice versa – write 'True' or 'False' against the statement.

1

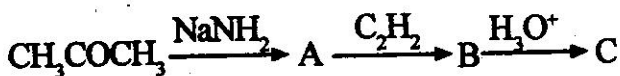
- (f) Predict the products and write the mechanism for each of the following reactions : 2×2



GROUP— A(b)

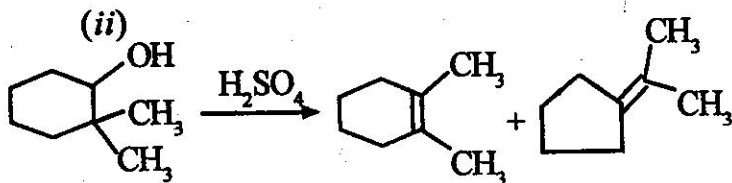
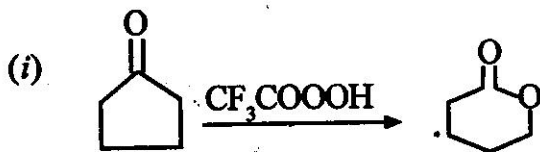
Answer any two questions : 10×2

3. (a) Identify A, B and C and show mechanism of the formation of B only : 3

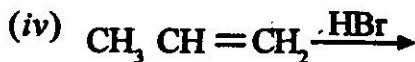
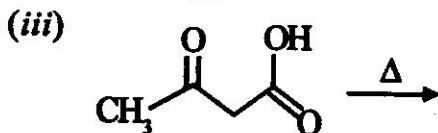
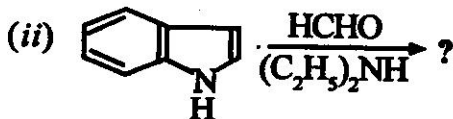
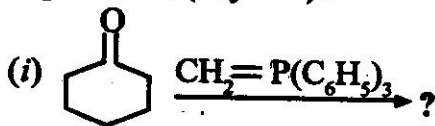


- (b) How can you show that Hofmann, Curtius, Lossen and Schmidt reaction proceed through a common intermediate? Give proper evidence for justification of your answer. 3

- (c) Discuss mechanism of the following transformation : 2×2



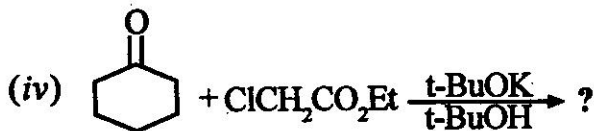
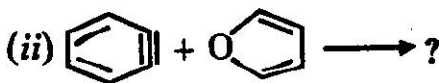
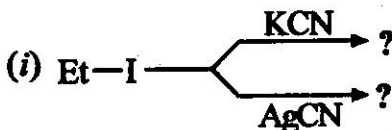
4. (a) Apply Diels-Alder reaction for the synthesis of anthracene. Starting from anthracene how would you obtain 9-bromo anthracene? Explain the reaction. 4
- (b) Both *cis*- and *trans*-4-hydroxy cyclohexane-1-carboxylic acids are separately heated. Indicate the structural changes, if any. 2
- (c) Complete the following reactions with proper explanation (any two): 2 × 2



5. (a) What are π and σ -complexes in aromatic electrophilic substitution? 2

(b) The rate of the reaction of 1-bromobutane with azide ion is increased 5×10^3 fold on changing the solvent from methanol to acetonitrile. 3

(c) Predict the products with mechanism in the following reactions (any two): $2\frac{1}{2} \times 2$



6. (a) Trans-4-t-butylcyclohexane-1-tosylate gives rise to 4-t-butylcyclohexane with Sph^{\ominus} rather than OEt^{\ominus} . Justify. 2

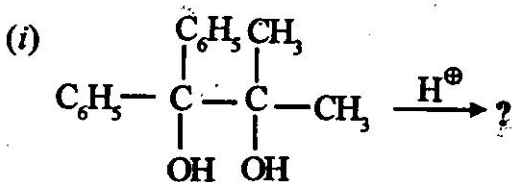
(b) Write the A_{Ac2} and B_{Ac2} mechanism for the

hydrolysis of methyl benzoate. It is observed that electron withdrawing substituents in the m- and p-positions enhance the rates of B_{Ac^2} hydrolysis of substituted methyl benzoate while the effect is negligible for A_{Ac^2} reactions. 4

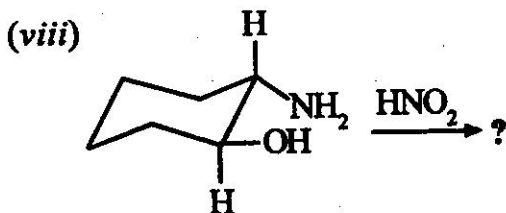
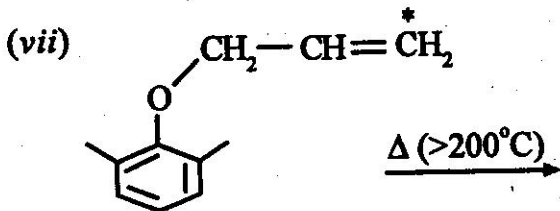
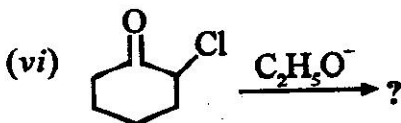
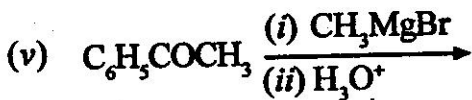
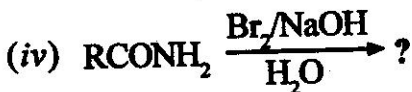
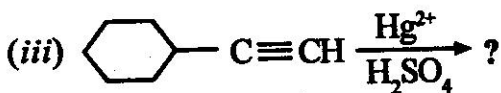
- (c) A hydrocarbon which has the molecular formula C_6H_{12} , was subjected to ozonolysis giving equimolar amounts of ethyl methyl ketone ($CH_3CH_2COCH_3$) and acetaldehyde (CH_3CHO). Assign structure to it. 2
- (d) Show how deuterium labelling experiment may be used to verify the mechanism of Cannizzaro reaction. 2

GROUP— A(c)

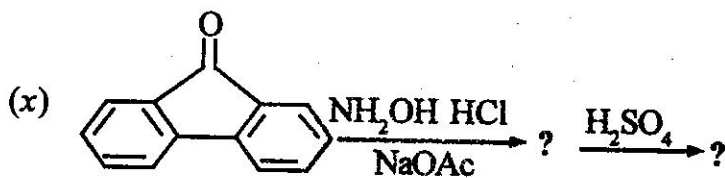
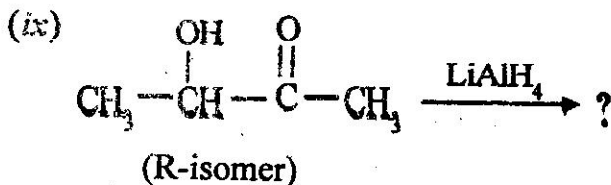
7. Complete the following giving mechanism (any five): 2 × 5



(9)



(10)



GROUP-B

(Inorganic)

GROUP-B(a)

Answer any one question : 15×1

8. (a) State the uncertainty principle and explain the situations in which it becomes insignificant.

$$1\frac{1}{2} + 1\frac{1}{2}$$

- (b) Calculate the amount of energy necessary for $\text{He}^+ \rightarrow \text{He}^{2+} + e$ in gaseous form.

[given, I.P. of H(ground state) = 2.18×10^{-18} Joule/atom.]

3

- (c) Explain the origin of black body radiation, Using quantum theory. 2
- (d) Compare the structure of XeO_4 and XeO_2F_2 . 3
- (e) What are pseudohalogens? 2
- (f) The formula of sulphuric acid in H_2SO_4 but the formula of telluric acid is H_6TeO_6 - Explain. 2
9. (a) Calculate the equilibrium constant for the reaction $-\text{Fe}^{2+} + \text{Cl}^{4+} = \text{Fe}^{3+} + \text{Ce}^{3+}$ at 298 K
Given $- [E^\circ_{\text{Cl}^{4+}/\text{Cl}^{3+}} = 1.28 \text{ V in } 1 \text{ (M) HCl}]$. 3
- (b) The E° values of $\text{Cu}^{2+} / \text{Cu}^+$ (0.15 V) and I/I^- (0.54 V) indicates that I_2 should not be liberated by the reaction of iodide and Cu^{2+} . But this is a common reaction - How is this fact possible. 3
- (c) "ClO₂ has no tendency to dimerize but NO₂ can easily be dimerized" - Explain. 2
- (d) Calculate the lowest wave length in Lyman series in hydrogen atomic spectrum.
[given $R = 109678 \text{ cm}^{-1}$] 3

- (e) What happens when XeO_3 is reacted with iodine in acid medium. 2
- (f) What is dioxygenyl compound? Given one example. 2

GROUP-B(b)

Answer any two questions : 10 × 2

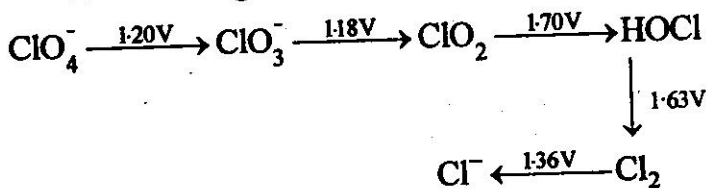
10. (a) 1 gm of ^{226}Ra emits 11.6×10^7 α particles per year. Calculate the value of Avogadro number (No) [given $t_{1/2} = 1590 \text{ Y}$] 3
- (b) What happens when XeO_3 is reacted with NaOH? 2
- (c) Show that the equilibrium constant K of a redox process is given by the equation

$$\log K = \frac{n_1 n_2}{0.059} (E_1^\circ - E_2^\circ),$$

where the terms have their usual significance. 3

- (d) Explain why SF_6 is unreactive towards water but TeF_6 is readily hydrolyzed. 2

11. (a) Define 'Magic number'. Why such number shows high nuclear stability? 3
- (b) Write short note on 'Basic property of halogen'. 3
- (c) Draw the Frost diagram from the following Latimer diagram 4



12. (a) Explain SO_3 is planar but SO_3^{2-} is pyramidal. 2
- (b) What happens when urea is heated with anhydrous sulphuric acid? 2
- (c) Calculate the binding energy per nucleon in ${}^{56}_{26}\text{Fe}$ whose atomic mass is 55.9571 amu, (mass of proton = 1.0081 amu, mass of neutron = 1.009 amu). 3
- (d) Write short notes on radioactive equilibrium. 3

13. (a) What is nuclear isomerism ? 2
- (b) What is the role of MnSO_4 in Zimmermann-Reinhardt solution. 2
- (c) Write note on S_4N_4 with respect to its synthesis and structure. $1\frac{1}{2} + 1\frac{1}{2}$
- (d) Packing fraction may be positive or negative whereas mass defect is not— Explain. 3

GROUP—B(c)

Answer any five questions : 2×5

14. (a) What is the significance of (-)ve sign in the energy expression of an electron in hydrogen like system ?
- (b) Briefly explain the importance of ozone layer in our atmosphere.
- (c) The highest fluoride of oxygen is OF_2 whereas, for sulphur it is SF_6 — Comment.
- (d) Compare the structure of XeF_5 and XeF_6 .

- (e) The ratio of number of neutron and proton is related to the stability of the nucleus—
Explain.
- (f) Arrange the oxyacids of chlorine in order of Their increasing acidity.
- (g) What is de Broglie relationship? How de Broglie's equation can be used to explain Bohr's atomic model?
-