2019

B.Sc.

2nd Semester Examination

CHEMISTRY (Honours)

Paper - C4T

Full Marks : 40 Time : 2 Hours

The figures in the margin indicate full marks.
Candidates are required to give their answers in their own words as far as practicable.

Group - A

1. Answer any *five* questions : 2×5=10

(a) Butane - 2, 3 - dione remains almost cent per cent in the keto form but cyclopentane 1, 2 - dione remains almost cent percent in enol form — explain.

(b) Quinuclidine shows more basic character than triethylamine towards triethylborane — explain.

(c) Either *MeCH(OH) CH_2SEt* (*a*) or *MeCH(SEt) CH_2CH* (*b*) produces the same products on

[Turn Over]

treatment with dry *HCl*. Give the mechanisms involved.

(d) Which one of the following solvents will be the best for the reaction between 1° bromide and *KCN* ? H_2O, Me_2CO and *DMSO*.

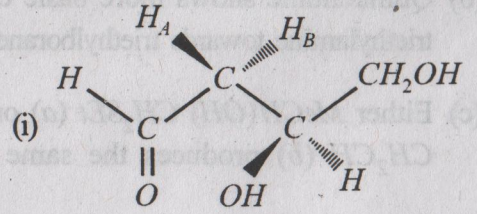
(e) Draw the more stable conformation of 1 - bromopropane and explain the reason of that stability.

(f) *D* and *L* stereoisomers are not necessarily enantiomers. Illustrate your answer with a suitable example.

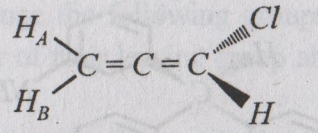
(g) Show K.C.P. and T.C.P. with explanation for the tautomerisation of phenyl nitromethane in presence of alkali followed by acidification with *HCl*.

(h) State whether the marked hydrogens are homotopic, enantiotopic or diastereotopic —

(i)



(ii)



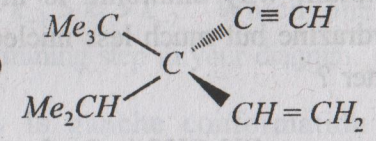
Group - B

2. Answer any *four* questions. 4×5=20

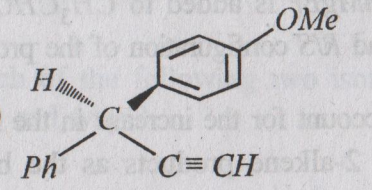
(a) Draw the energy profile diagram of one of the three isomers of butane 2, 3 diol about rotation against C_2 - C_3 bond. 2

(b) Write down the R/S descriptors showing priority sequence of each atom or group —

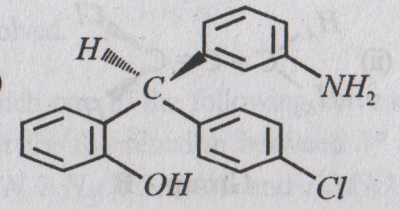
(i)



(ii)



[Turn Over]

(iii) 

1+1+1=3

3. (a) [18] - crown - 6 greatly increases the rate of an SN^2 reaction between potassium cyanide and benzyl bromide — explain. 1½

(b) What products do you expect when (+) erythro form of 3 - bromobutan - 2 - *Cl* is treated with dilute alkali ? Give mechanism also. 2

(c) Explain why ammonia is more basic than hydrazine but much less nucleophilic than the latter ? 1½

4. (a) Represent CH_3CHO in Re-face. If one mole of *PhMgBr* is added to CH_3CHO from Re-face, find *R/S* configuration of the product. 1½

(b) Account for the increase in the ratio of 1-alkene to 2-alkene products as the base is changed from $MeO^{\ominus}$ to $Me_3CO^{\ominus}$ to $Et_3CO^{\ominus}$ in the dehydrobromination of 2 - bromo - 2, 3 - dimethylbutane. 2

(c) Arrange the following groups in an increasing order of their leaving group ability (with reason)

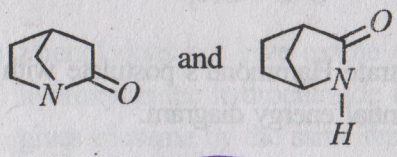
$p-CH_3-C_6H_4SO_3^{\ominus}$, $PhO^{\ominus}$, $P-NO_2C_6H_4O^{\ominus}$

1½

5. (a) Construct an energy profile diagram for a reaction $A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} C$ in which the relative stabilities are $C > A > B$ and for which the relative four rate constants are $k_2 > k_{-1} > k_1 > k_{-2}$. Which one is the rate determining step in your diagram. 2

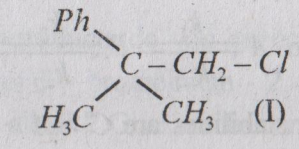
(b) Why is ganche conformation of ethylene chlorohydrin is favoured over anti-conformation ? 1½

(c) Which of the following two isomers is more basic and why ? 1½



6. (a) Pentane 2, 4 dione dissolves in aqueous *NaOH* solution and gives red colouration with aqueous feric chloride solution but bicyclo [2.2.2] octane - 2, 6 - dione does not respond to these tests — explain. 1½

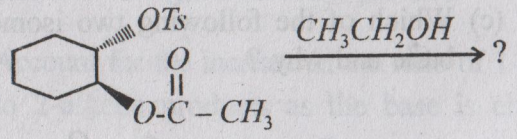
(b) The chloride (I) undergoes SN^1 solvolysis reaction many thousand times faster than neopentyl chloride — explain. 1½



(I)

(c) Explain the differences between pK_1 and pK_2 values of saturated dicarboxylic acids, Why does this difference decrease with the increase in the chain length ? 1+1=2

7. (a) Predict the product with mechanism— 2



(b) Illustrate Hammond's postulate with reference to potential energy diagram. 2

(c) What do you mean by valence tantomerism ? Give an example. 1

Group - C

Answer any *one* question. 1×10=10

8. (a) Optically pure (*R*) - enantiomer of 1-phenylethanol is separately treated with (i) *p - TsCl* followed by $EtO^{\ominus}K^{\oplus}$ (ii) *K* followed by *EtOTs*. Identify the products. 1½+1½

(b) What is the basic structural requirement for the presence of a pseudoasymmetric centre in an acyclic compound ? 1½

(c) Explain this statement : chirality of a molecule is a dimension-dependent property. 1½

(d) What is the major product of the pyrolysis of $Me_2CHCH(Me)OAc$? Give reasons in favour of your answer. 2

(e) What is the *P*, *M* system of nomenclature of substituted ethanes and compounds containing axial chirality ? Give appropriate examples. 2

9. (a) Cl^- is a better nucleophile than Br^- in *DMSO* but not in water-explain. 1½

(b) Phenol does not give oxime on treatment with hydroxylamine hydrochloride but phloroglucinol gives trioxime by the same reaction-explain, 1½

[Turn Over]

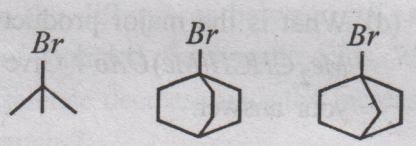
(c) What are the conditions for chiralily in biphenyls ? 1

(d) State the principal reason for different rates of the following two related reactions—

$$N_3^{\ominus} + CH_3Cl \xrightarrow{\text{slower}} CH_3N_3 + \overset{\ominus}{Cl}$$

$$N_3^{\ominus} + CH_3I \xrightarrow{\text{faster}} CH_3N_3 + I^{\ominus}$$ 2

(e) Rate of solvolysis of the bromides (a), (b) and (c) in 80% ethanol at 25°C are $1 : 10^{-6} : 10^{-14}$. Explain the reason for these relative rates. 2



(a) (b) (c)

(f) What do you mean by secondary kinetic isotopic effect ? How does it differ fro primary kinetic isotopic effect ? Explain with suitable examples. 2