

2019

B.Sc.

2nd Semester Examination
CHEMISTRY (Honours)

Paper - C4T

Full Marks : 40

Time : 2 Hours

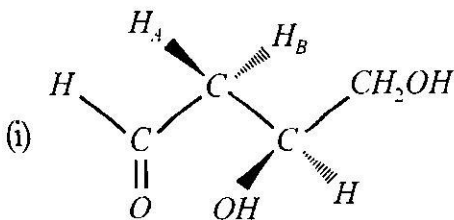
*The figures in the margin indicate full marks.
Candidates are required to give their answers
in their own words as far as practicable.*

Group - A

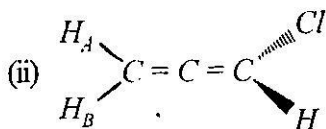
1. Answer any *five* questions : 2×5=10
- (a) Butane - 2, 3 - dione remains almost cent per cent in the keto form but cyclopentane 1, 2 - dione remains almost cent percent in enol form — explain.
- (b) Quinuclidine shows more basic character than triethylamine towards triethylborane — explain.
- (c) Either $MeCH(OH)CH_2SEt$ (a) or $MeCH(SEt)CH_2CH$ (b) produces the same products on

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- 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 —



(3)



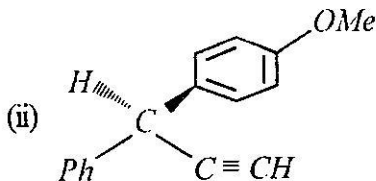
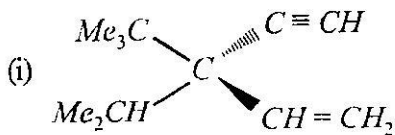
Group - B

2. Answer any *four* questions.

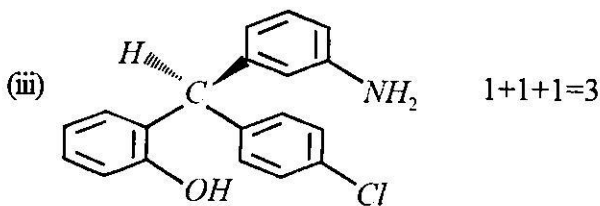
4×5=20

(a) Draw the energy profile diagram of one of the three isomers of butane 2, 3 diol about rotation against C₂ - C₃ bond. 2

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

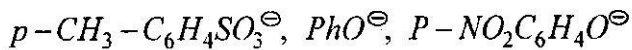


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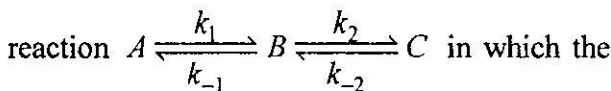
3. (a) [18] - crown - 6 greatly increases the rate of an S_N2 reaction between potassium cyanide and benzyl bromide — explain. $1\frac{1}{2}$
- (b) What products do you expect when (+) erythro form of 3 - bromobutan - 2 - *Cl* is treated with dilute alkali ? Give mechanism also. 2
- (c) Explain why ammonia is more basic than hydrazine but much less nucleophilic than the latter ? $1\frac{1}{2}$
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. $1\frac{1}{2}$
- (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)



1½

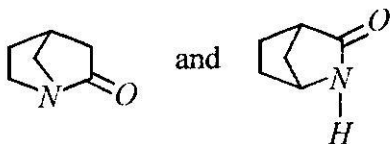
5. (a) Construct an energy profile diagram for a



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 gauche conformation of ethylene chlorohydrin is favoured over anti-conformation? 1½

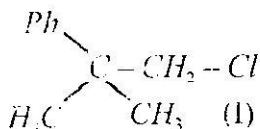
- (c) Which of the following two isomers is more basic and why? 1½



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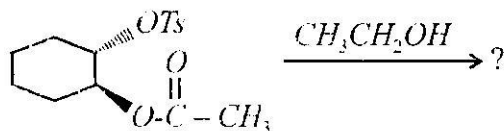
6. (a) Pentane 2, 4 dione dissolves in aqueous $NaOH$ solution and gives red colouration with aqueous feric chloride solution but bicyclo [2.2.2] octane - 2, 6 - dione does not respond to these tests — explain. $1\frac{1}{2}$

- (b) The chloride (I) undergoes SN^1 solvolysis reaction many thousand times faster than n-pentyl chloride — explain. $1\frac{1}{2}$



- (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 tautomerism? Give an example. 1

Group - C

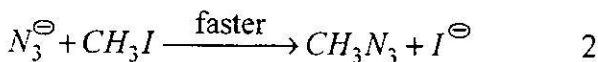
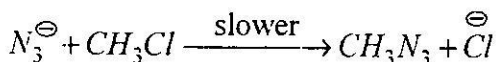
Answer any *one* question. $1 \times 10 = 10$

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. $1\frac{1}{2} + 1\frac{1}{2}$
- (b) What is the basic structural requirement for the presence of a pseudoasymmetric centre in an acyclic compound ? $1\frac{1}{2}$
- (c) Explain this statement : chirality of a molecule is a dimension-dependent property. $1\frac{1}{2}$
- (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. $1\frac{1}{2}$
- (b) Phenol does not give oxime on treatment with hydroxylamine hydrochloride but phloroglucinol gives trioxime by the same reaction-explain, $1\frac{1}{2}$

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

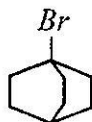
(d) State the principal reason for different rates of the following two related reactions—



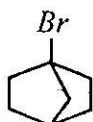
(e) Rate of solvolysis of the bromides (a), (b) and (c) in 80% ethanol at 25°C are 1 : 10⁻⁶ : 10⁻¹⁴. Explain the reason for these relative rates. 2



(a)



(b)



(c)

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