

2019

B.Sc.

2nd Semester Examination  
**CHEMISTRY (Honours)**

Paper - C4T

Full Marks : 40

Time : 2 Hours

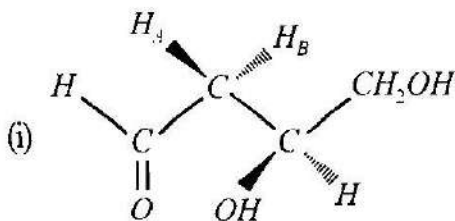
*The figures in the margin indicate full marks.  
Candidates are required to give their answers  
in their own words as far as practicable.*

**Group - A**

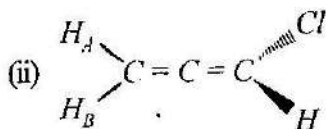
1. Answer any *five* questions : 2×5=10
- (a) Butane - 2, 3 - dione remains almost cent per cent in the keto form but cyclopentane 1, 2 - dione remains almost cent percent in enol form — explain.
- (b) Quinuclidine shows more basic character than triethylamine towards triethylborane — explain.
- (c) 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  $1^\circ$  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 —



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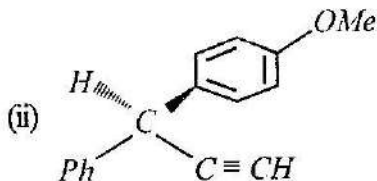
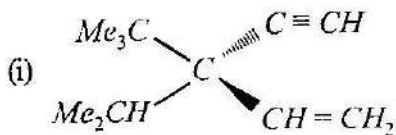
**Group - B**

2. Answer any *four* questions.

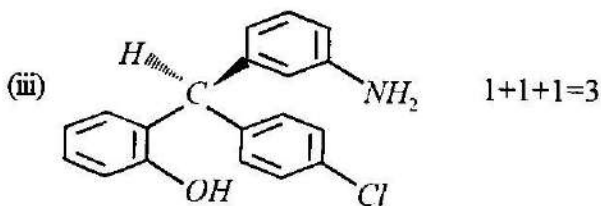
4×5=20

(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 —

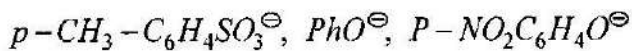


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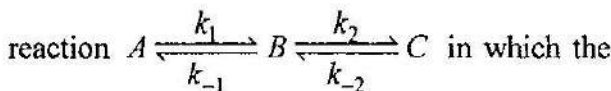
3. (a) [18] - crown - 6 greatly increases the rate of an  $S_N2$  reaction between potassium cyanide and benzyl bromide — explain.  $1\frac{1}{2}$
- (b) What products do you expect when (+) erythro form of 3 - bromobutan - 2 - *Cl* is treated with dilute alkali ? Give mechanism also. 2
- (c) Explain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

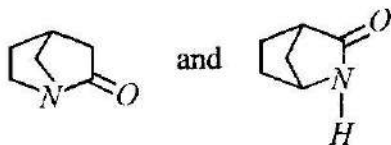
5. (a) Construct an energy profile diagram for a



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

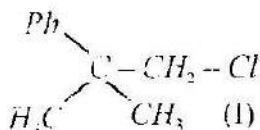
- (c) Which of the following two isomers is more basic and why? 1½



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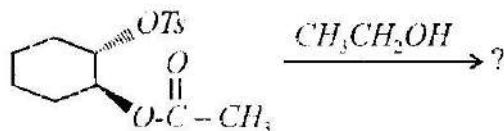
6. (a) Pentane 2, 4 dione dissolves in aqueous  $NaOH$  solution and gives red colouration with aqueous feric chloride solution but bicyclo [2.2.2] octane - 2, 6 - dione does not respond to these tests — explain. 1½

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



- (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

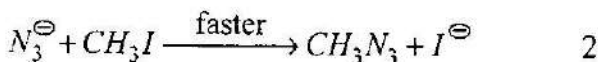
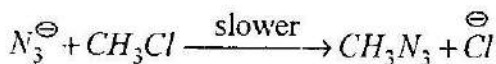
Answer any *one* question.  $1 \times 10 = 10$

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.  $1\frac{1}{2}$

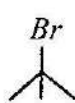
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(c) What are the conditions for chirality in biphenyls? 1

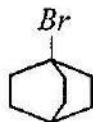
(d) State the principal reason for different rates of the following two related reactions—



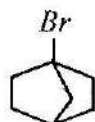
(e) Rate of solvolysis of the bromides (a), (b) and (c) in 80% ethanol at 25°C are 1 : 10<sup>-6</sup> : 10<sup>-14</sup>. Explain the reason for these relative rates. 2



(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