# 2018

## **CHEMISTRY - HONOURS**

# First Paper

(Group - A)

Full Marks: 50

The figures in the margin indicate full marks.

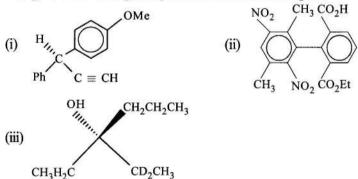
Candidates are required to give their answers in their own words as far as practicable.

CHT - 12a

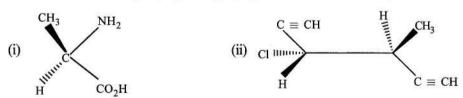
#### Unit - I

Answer any three questions.

1. (a) Assign the following compounds with R/S descriptor:



(b) Convert the following Flying-Wedge projections to Fischer Projections :



- 2. (a) Optically pure S (+)-2-bromooctane,  $[\alpha]_D^{25^\circ} = +36^\circ$ , reacts with aqueous NaOH in acetone to give optically pure R(-)-2-octanol,  $[\alpha]_D^{25^\circ} = -10.3^\circ$ , with partially racemised 2-bromooctanol whose  $[\alpha]_D^{25^\circ}$  is  $+30^\circ$ . If the specific rotation of the alcohol (product)  $[\alpha]_D^{25^\circ} = 6^\circ$ , calculate:
  - (i) % of inversion on and racemisation
  - (ii) % composition of each product

Please Turn Over

3+2

#### K(I)-Chemistry-H-1A

(2)

- (b) The pro-R hydrogen of chloroacetic acid is substituted by bromine with inversion of configuration. Predict the configuration of the final product showing the pro-R hydrogen of the original substrate.
- 3. (a) Give example/write down the structures of the following:
  - (i) a chiral molecule having a C2 axis.
  - (ii) 2R,  $3r^*$ , 4S 1, 2, 3, 4, 5 pentachloropentane.
  - (iii) syn-CH<sub>3</sub>CH (OH) CH (CH<sub>3</sub>) COPh
  - (b) Depict the most stable conformers of 1, 2-dichloroethane and 1, 2-difluoroethane and give reason of your answer.

    3+2
- 4. (a) Label the following pairs of molecules as homomers, enantiomers and diastereoisomers.

- (b) Write down the configuration of final product when R-2-hydroxypropanal is allowed to react with CH<sub>3</sub>MgBr where attack takes place from the Re-face and the immediate product thus formed is hydrolysed.
- 5. (a) Explain whether the following compounds are resolvable or not.

(b) Designate H<sub>A</sub> and H<sub>B</sub> in each of the following compounds as homotopic, enantiotopic or diastereotopic and explain: 3+2

(i) 
$$HO$$
  $CH_2 - HA$   $HA$   $HA$   $CH_2OH$   $CH_2OH$   $CH_2OH$   $CH_2OH$   $CH_2OH$ 

#### Unit - II

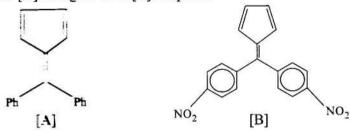
#### Answer any two questions.

- 6. (a) Draw the M.O.S of 1. 3-cyclobutadiene showing the nodes. Mention HOMO and LUMO in ground state.
  - (b) Compare the melting and boiling temperature of n-pentane and neopentane.

3+2

- 7. (a) Which method between heat of hydrogenation and heat of combustion is more susceptible to get the relative stabilities among 1-butene, E and Z-2-butene and isobutene? Justify your answer.
  - (b) Dipole moment of [A] is higher than [B]. Explain.

3+2



8. (a) Identify [B] and [C] and comment on aromaticity of [A], [B] and [C]



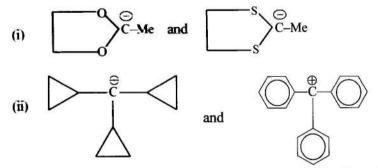
(b) Which diastereoisomer of stilbene dichloride shows higher dipole moment and why? 3+2

#### CHT - 12b

## Unit - I

Answer any three questions.

9. (a) Comment on the stability of the following pairs with reason.



(b) Any ortho hydroxy benzoic acid in stronger acid than benzoic acid. Explain.

3+2

- 10. (a) Draw the energy profile diagram of a two-steps exothermic reaction where activation energy of the 1st step is greater than that of 2nd step but the 2nd step is rate determining step. Justify your drawing.
  - (b) Compare the enol content of the following two compounds.— Justify.

3+2

11. (a) Compare the strength of the following compounds. Give reasons.

(b) Give an example each of electrophilic carbene and nucleophilic carbene.

3+2

- 12. (a) What do you mean by PKIE? How PKIE helps us to determine the source of 2nd hydrogen of the product alcohol in Cannizaro reaction?
  - (b) What is captidative radical? Explain with an example.

3+2

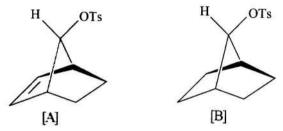
- 13. (a) When cis-2-butene and trans-2-butene separately react with CH<sub>2</sub>I<sub>2</sub> in presence of Zn-Cu couple, both cis and trans products are obtained. Predict the products and give reason.
  - (b) Arrange F<sup>-</sup>, Cl<sup>-</sup>, Br<sup>-</sup> and I<sup>-</sup> ions in decreasing order of their basicity and nucleophilicity (both in protic and aprotic solvents).
    3+2

#### Unit - II

#### Answer any two questions.

14. (a) Explain the following observation:

- (b) Which one will react faster in  $S_N1$  reaction,  $CH_2 = CHCH_2C1$  or,  $Ph_3C-C1$ ? Why? 3+2
- 15. (a) Compound [A] undergoes acetolysis at a rate 10<sup>11</sup> times faster than compound [B] with retention of configuration. Explain.



(b) Write the B<sub>AC</sub>2 mechanism of hydrolysis of

R — COOEt. Hence, arrange the following substituted esters in order of decreasing rates of hydrolysis (where, 
$$R = -OMe$$
,  $-NO_2$ ,  $-Cl$ ) with proper explanation.

- 16. (a) What are the possible reactive sites of the bromoester, BrCH<sub>2</sub>CH<sub>2</sub>COOEt, with respect to a nucleophile? With diethylamine as nucleophile suggest the structure of the major product.
  - (b) Identify [A], [B] and [C] with reasons, in brief:

(i) 
$$O^{\Theta}Na^{\Theta}$$
 +  $PhCH_2Br$   $DMSO$  [B]

(ii) MeO 
$$\longrightarrow$$
 CH<sub>2</sub>CH<sub>2</sub>OT<sub>S</sub>  $\xrightarrow{\text{NaOAC}}$  [C]