## U.G. 1st Semester Examination - 2020 CHEMISTRY [HONOURS]

**Course Code: CHEM-H-CC-T-02** 

Full Marks : 40 Time :  $2\frac{1}{2}$  Hours

The figures in the right-hand margin indicate marks.

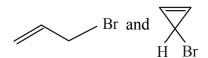
Candidates are required to give their answers in their own words as far as practicable.

- 1. Answer any **five** questions:
  - a) Calculate the double bond equivalent of the compound having molecular formula C<sub>3</sub>H<sub>7</sub>N and write down the structures that conform to this double bond equivalent.
  - b) n-butyl alcohol has much higher boiling point (118°C) than its isomers isobutyl alcohol (108°C) and diethyl ether (35°C).
  - c) Draw the different canonical forms of the following species indicating the most important contributor towards resonance hybrid:

$$CH_3OCH = CH - \overset{\oplus}{C}H_2$$

- d) Draw the Fischer Projection formula of
  - i) (2R, 3S)-3-Phenyl-2-butanol
  - ii) (R)-2-Deuteropropanoic acid.
- e) Explain why C=O bond energy in ketones is greater than the C-O bond energy in ethanol?
- f) (+) 1-Phenyl ethyl alcohol looses its optical activity in presence of acid— explain.
- g) Arrange the following in order of decreasing nucleophilicity with proper reasons:

h) Which one of the following compounds would undergo Ag<sup>+</sup> ion assisted hydrolysis at a faster rate and why:



2. Answer any **two** questions:

- $5 \times 2 = 10$
- a) i) Compare the dipole moment in each of the following pairs:
  - A) Butanal and 2-butenal
  - B) Vinyl chloride and ethyl chloride

 $2 \times 5 = 10$ 

ii) Draw all possible stereoisomers of EtCH = CH - CH - CH = CHEt

and comment on their optical activity.

2+3

b) i) Compare C-O bond distance in

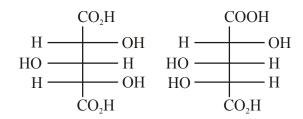
$$Me_2C=O$$
,  $MeCO_2^-$  and  $Me$ 

ii) Assign R/S designation to the following compounds:

- c) i) Write down the basic difference between resonance effect and electromeric effect. Explain with suitable examples.
  - ii) Draw the  $\pi$ -M.O. pictures of LUMO of 1,3,5-hexatriene and HOMO of allyl radical in the ground state. 3+2

- d) i) Depict the symmetry elements of the following molecules in terms of  $\sigma$  and  $C_n$ :
  - A) Cis-1,3-dimethyl cyclobutane
  - B) trans-1,2-dibromo ethene
  - ii) Dimethoxy carbene is reluctant to add to isobutene– explain. 3+2
- 3. Answer any **two** questions:  $10 \times 2 = 20$ 
  - a) i) Label the C-3 centres of the following molecules as stereogenic/non-stereogenic and chirotopic/achirotopic.

    Justify your answer.



- ii) Outline the reaction steps you would employ to carry out the resolution of a racemic alcohol.
- iii) A good base is not necessarily a good nucleophile— explain.

iv) Which of the following ions are the ambident nucleophiles:

- b) i) What is benzyne? Give chemical evidence in favour of formation of the benzyne as reactive intermediate.
  - ii) 1,3,5-cycloheptatriene is not aromatic whereas its derivative tropolone (A) behaves like a typical phenol– why?

$$\bigcup_{(A)}^{O} OH$$

- iii) Justify the statement- s<sub>2</sub> and i are equivalent operations.
- iv) Show that cyclopentadienyl cation is a diradical. 3+2+3+2
- c) i) Identify whether the following pairs of compounds represent enantiomers, diastereoisomers and homomers:

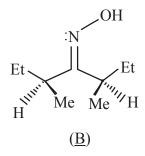
$$C) \qquad \begin{matrix} Me \\ Me \\ H \end{matrix} \qquad \begin{matrix} Me \\ H \end{matrix} \qquad \begin{matrix} H \\ Me \end{matrix} \qquad \begin{matrix} H \\ H \end{matrix}$$

- the specific rotation of a mixture containing 12gm of (+)-2-butanol and 8gm of (-)-2-butanol. The specific rotation of enantiomerically pure (+)-2-butanol is +13.5°.
- iii) Chloride ion in  $Bu_4N^+Cl^-$  in acetone is a better nucleophile than that in LiCl in the same solvent— explain.
- iv) Why acyl halides are more reactive towards water than alkyl halides?

3+3+2+2

187/Chem. (5) [*Turn over*]

d) i) Does the following oxime(B) show optical activity and E-Z isomerism? Label the configurations of the chiral centres of B.



- ii) Is it possible to separate the carbanion  $\operatorname{Et} \overset{\circ}{C} HMe$  into enantiomers?
- iii) Compare the electron density at the marked carbon atoms of each of the following pairs and rationalize:

A) 
$$Me$$
 $Me$ 
 $Me$ 
 $Me$ 
 $Me$ 
 $Me$ 
 $Me$ 
 $Me$ 

$$CH_{2}CH_{3} \qquad H_{3}C-C-CH_{3}$$

$$B) \qquad and \qquad *$$

iv) Comment on the aromaticity of the following compounds C and D:

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187/Chem. (7) [*Turn over*]

187/Chem.

(8)