## 2019

## CHEMISTRY

(Major)

Paper: 1.2

## ( Organic Chemistry )

Full Marks: 60

Time: 3 hours

The figures in the margin indicate full marks for the questions

1. Answer the following questions:

 $1 \times 7 = 7$ 

(a) Arrange the C—H bond lengths in increasing order:

$$C-H$$
,  $C-H$ ,  $C-H$   
 $sp^3$   $sp^2$   $sp$ 

- (b) Why is the boiling point of n-pentane more than neopentane?
- (c) Why is acetic acid a stronger acid than propanoic acid?

- (d) Why does pentane-2,4-dione mostly exist in the enol-form?
- (e) Assign R- or S-configuration for the molecule:

- (f) What is the state of hybridization of carbon in CH<sub>2</sub>—NO<sub>2</sub>?
- (g) Why is the dipole moment of orthodichlorobenzene not zero?

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2. Answer any four of the following questions:

 $2 \times 4 = 8$ 

- (a) Draw the Newman projections for all the conformers that result from rotation about the C-2 and C-3 bonds of butane and identify the most stable amongst them.
- (b) Draw and label the E- and Z-isomers of 1,2-dichloro-3-ethyl-4-methyl-2pentene.
- (c) Between ortho-nitrophenol and paranitrophenol, which has higher boiling point and why?

- (d) Explain why Ph S CI reacts with water 100 times faster than Cl.
- (e) Which of the following carbocations is more stable and why?

e stable and why?

$$CH_2=CH-CH_2$$

- 3. Answer any three of the following questions:
  5×3=15
  - (a) What do you mean by kinetically controlled and thermodynamically controlled reactions? Draw the energy profile diagram for these two reactions.
    2+3=5

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2+3=5

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- (b) (i) What is  $S_N 2$  mechanism? Give an example to explain it. 1+1=2
- (ii) Explain why trans-2-chlorocyclohexanol gives epoxycyclohexane in high yield on treatment with a base whereas the cis-isomer does not react with the base.

(c) What are non-classical carbocations?

Give example of it. Discuss the stability
of non-classical carbocations. 1+1+3=5

(Turn Over)

- (d) Why is it difficult to separate racemic mixture? Describe a method of resolving a racemic mixture. 1½+3½=5
- (e) What is atropisomerism? What types of isomerism are shown by 3-bromopent-2-ene? Give their structures along with their designation. Why are enantiomers not easily separated?

1+1+2+1=5

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- 4. Answer either (a) or (b), (c) or (d) and (e) or (f) from the following questions: 10×3=30
  - (a) (i) Explain why C—N bond length in methylamine is more than that in urea.
  - (ii) What is hyperconjugation and what are its types? What are the conditions for any organic species to exhibit hyperconjugation? 1+2+2=5
  - (iii) Arrange the following  $C_a C_b$  bond lengths in increasing order and explain the observation:

 $CH_3-C_a=C_b-CH_3$ ,  $CH_2=C_aH-C_bH=CH_2$ ,

 $CH_3-C_aH_2-C_bH_2-CH_3$ 

(b) (i) What is  $pK_a$ ? How is it related to acid strength? Explain why  $pK_a$ -value of picric acid is much lower than phenol. 1+1+2=4

- (ii) What is diagonal hybridization?
  What are its characteristics? 1+2=3
- (iii) What is inductive effect? What are its applications in determining the stability of carbocations? 1+2=3
- (c) (i) Which of the two alkenes, 1-pentene or 2-pentene on reaction with HBr will produce 2-bromopentane exclusively? Explain the reason.
  - (ii) How can you generate carbocations? Arrange the following carbocations in increasing order of stability and explain the reasons:

- (iii) Write a reaction to show evidence that  $S_N 1$  mechanism involves carbocation intermediate.
- (d) (i) What are pyrolytic eliminations?

  Give an example. Propose a mechanism for the pyrolytic elimination reaction. 1+1+3=5

(Turn Over)

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- (ii) Write a general mechanism for elimination reactions proceeding via the El pathway. Provide two evidences in support of the mechanism.
  - (e) (i) Explain why the chair-conformation of cyclohexane is more stable than the boat-conformation. Which conformer of cis-1,3-cyclohexanediol is more stable and why? 3+2=5
    - (ii) How many stereoisomers are there for 2,3-diphenylbutane? Use Fischer projection formulas to draw all the stereoisomers and assign R-or S-designation to the asymmetric carbon atoms. Indicate the structures which are optically active. 1+3+1=5
  - (f) (i) Explain why benzylchloride is more reactive than alkyl chloride in nucleophilic substitution.
    - (ii) Give the products A, B, C and D in the following reactions:  $1 \times 2 = 2$
  - (1)  $CH_3CHO \xrightarrow{aq. NaOH} A \xrightarrow{\Delta} B$

(2) 
$$\bigcirc CCOR \xrightarrow{\text{anh. AlCl}_3} C + D$$

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(iii) Olefinic double bonds are prone to electrophilic addition whereas carbonyl C=O bonds are prone to nucleophilic addition. Explain.

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(iv) Explain why elimination reactions always complete with substitution reaction.

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