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 : 1×7=7

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

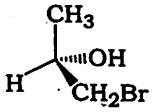
$$\underset{sp^3}{C—H},\ \underset{sp^2}{C—H},\ \underset{sp}{C—H}$$

(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 $\overset{\ominus}{C}H_2—NO_2$?

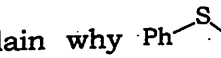
(g) Why is the dipole moment of *ortho*-dichlorobenzene not zero?

2. Answer any *four* of the following questions : 2×4=8

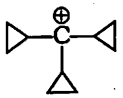
(a) Draw the Newman projections for all the conformers that result from rotation about the C-2 and C-3 bonds of butane and identify the most stable amongst them.

(b) Draw and label the *E*- and *Z*-isomers of 1,2-dichloro-3-ethyl-4-methyl-2-pentene.

(c) Between *ortho*-nitrophenol and *para*-nitrophenol, which has higher boiling point and why?

(d) Explain why  reacts with water 100 times faster than  .

(e) Which of the following carbocations is more stable and why?

 and $CH_2=CH—\overset{\oplus}{C}H_2$

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

(b) (i) What is S_N2 mechanism? Give an example to explain it. 1+1=2

(ii) Explain why *trans*-2-chloro-cyclohexanol gives epoxy-cyclohexane in high yield on treatment with a base whereas the *cis*-isomer does not react with the base. 3

(c) What are non-classical carbocations? Give example of it. Discuss the stability of non-classical carbocations. 1+1+3=5

(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

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. 2

(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 : 3

$CH_3—C_a\equiv C_b—CH_3$, $CH_2=C_aH—C_bH=CH_2$,

$CH_3—C_aH_2—C_bH_2—CH_3$

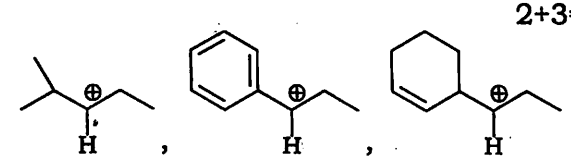
(b) (i) What is pK_a? How is it related to acid strength? Explain why pK_a-value of picric acid is much lower than phenol. 1+1+2=4

(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-bromo-pentane exclusively? Explain the reason. 3

(ii) How can you generate carbocations? Arrange the following carbocations in increasing order of stability and explain the reasons : 2+3=5



(iii) Write a reaction to show evidence that S_N1 mechanism involves carbocation intermediate. 2

(d) (i) What are pyrolytic eliminations? Give an example. Propose a mechanism for the pyrolytic elimination reaction. 1+1+3=5

(ii) Write a general mechanism for elimination reactions proceeding via the *E*1 pathway. Provide two evidences in support of the mechanism. 3+2=5

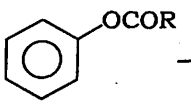
(e) (i) Explain why the chair-conformation of cyclohexane is more stable than the boat-conformation. Which conformer of cis-1,3-cyclohexane-diol is more stable and why? 3+2=5

(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. 2

(ii) Give the products *A*, *B*, *C* and *D* in the following reactions : 1×2=2

(1) $CH_3CHO \xrightarrow{\text{aq. NaOH}} A \xrightarrow{\Delta} B$

(2)  $\xrightarrow{\text{anh. } AlCl_3} C + D$

(Continued)

(iii) Olefinic double bonds are prone to electrophilic addition whereas carbonyl C=O bonds are prone to nucleophilic addition. Explain. 3

(iv) Explain why elimination reactions always complete with substitution reaction. 3

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