2012

CHEMISTRY

(Major)

Paper : 1.2

Full Marks : 60

Time : 2½ hours

The figures in the margin indicate full marks for the questions

1. Answer the following questions (any *seven*) : 1×7=7

(a) Draw the structural formula of 5,5-dimethyl-3-oxohexanoic acid.

(b) What is the hybridisation of each of the carbon atoms in an allene?

(c) In which of the two compounds OF_2 and NF_3, the bond angle is greater?

(d) Give one example of a compound which is optically active but does not contain a chiral centre.

(e) Name and give the structure of a free-radical inhibitor.

(f) Tropylium bromide is an ionic compound. Explain.

(g) Arrange the following in order of decreasing nucleophilicity :

$$NH_3, NH_2^-, R_2NH, R_2N^-$$

(h) In the reaction of 1-bromobutane with a base, which of the two bases EtO^- and $(CH_3)_3CO^-$ would lead to greater amount of the elimination product?

(i) Explain whether BF_4^- is a nucleophile or not.

2. Answer the following questions (any *four*) :

(a) Name a technique by which you can separate *ortho*-nitrophenol and *para*-nitrophenol. Which among the two has higher boiling point and why? ½+1½

(b) Classify the following as either aromatic, nonaromatic or antiaromatic. Give reasons : 1+1

(i) 

(ii) 

(Continued)

(c) Account for the fact that cyclopentadiene has $pK_a \approx 16$. 2

(d) Among pyridine and piperidine, which one is a stronger base and why? 1+1

(e) Draw the enantiomers of lactic acid and assign *R*, *S* designation. 1+1

3. Answer the following questions (any *three*) :

(a) Taking naphthalene as an example, explain what is partial bond fixation. Which bond phenanthrene is readily attacked by reagents and why? 3+2

(b) How many stereoisomers are observed for 2,3-diphenylbutane? Use Fischer 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

(c) How is a racemic mixture different from a mesocompound? Give examples to illustrate the differences. What do you mean by percent optical purity and optical purity? 2+1+2

(d) With the help of an example, explain what you mean by optical pumping. Draw structural formulas of 1-bromo-2-chloropropene and assign *E* or *Z* designation to the geometrical isomers. 3+2

(e) Why is the chair form of cyclohexane more stable than the boat form? Draw the various chair forms of methylcyclohexane. Identify the stable one and give reasons for your answer. 2+1+2

4. Answer the following questions (any *three*) :

(a) What are configurational and conformational isomers? Draw the possible conformers of *n*-butane. Designate each of the conformers. Arrange the conformers in order of decreasing stability. Identify the least stable conformer and assign reason for it being least stable. Draw the potential energy diagram to show the variation of energy for the various conformers. 2+2+1+1+2+2

(b) Which one is more reactive towards nucleophiles—acetaldehyde or acetone? Explain. What happens when acetaldehyde is allowed to react with

aq. NaOH? Propose a mechanism. What is the driving force for this reaction? Complete the following :

$$CH_3CHO + C_6H_5CHO \xrightarrow{NaOH\ (aq.)} ?$$

1+3+1+3+1+1

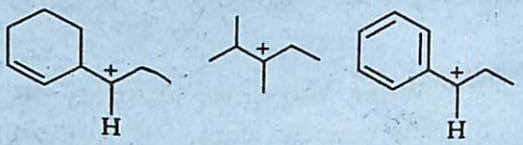
(c) "When *tert*-butyl chloride is allowed to react with water, it rapidly produces *tert*-butyl alcohol. The product is the result of a substitution of chloride by hydroxy group." Propose a mechanism and write the steps involved. Draw the energy-profile diagram. What would happen to the rate of the reaction if instead of *tert*-butyl chloride, *tert*-butyl iodide is taken and why? What would be the effect on the rate of the reaction if a small amount of NaCl is added from outside and why? Would you expect any change in the rate of the reaction if water is replaced by some other nucleophile?

3+2+2+2+1

(d) Discuss the mechanistic steps involved in an elimination reaction, proceeding by the E2 mechanism. Discuss the stereochemical evidence to support the E2 mechanism. With the help of examples, explain what is Hofmann elimination and Saytzeff elimination.

3+3+4

(e) What are carbocations? How can you generate carbocations? Arrange the following carbocations in decreasing order of stability and explain the reasons :



What are carbenes? Give the structures of the two types of carbenes. Give an example of a reaction which involves carbene as an intermediate. 1+2+3+1+2+1

(f) How do the following factors affect elimination versus substitution?

(i) Basicity versus nucleophilicity

(ii) Substrate structure

What are pyrolytic eliminations? Give an example. Propose a mechanism for the pyrolytic elimination reaction.

2½+2½+1+1+3

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