

2019

CHEMISTRY

(Major)

Paper : 1.2

(Organic Chemistry)

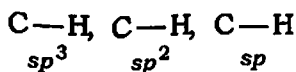
Full Marks : 60

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 :

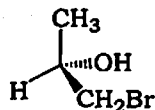


(b) Why is the boiling point of *n*-pentane more than neopentane?

(c) Why is acetic acid a stronger acid than propanoic acid?

(2)

- (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 $\overset{\ominus}{\text{C}}\text{H}_2\text{—NO}_2$?
- (g) Why is the dipole moment of *ortho*-dichlorobenzene not zero?

2. Answer any *four* of the following questions :

2×4=8

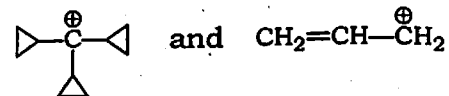
- (a) Draw the Newman projections for all the conformers that result from rotation about the C-2 and C-3 bonds of butane and identify the most stable amongst them.
- (b) Draw and label the *E*- and *Z*-isomers of 1,2-dichloro-3-ethyl-4-methyl-2-pentene.
- (c) Between *ortho*-nitrophenol and *para*-nitrophenol,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

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(Continued)

(3)

- (d) Explain why $\text{Ph—S—CH}_2\text{—CH}_2\text{—Cl}$ reacts with water 100 times faster than $\text{CH}_3\text{—CH}_2\text{—CH}_2\text{—Cl}$.
- (e) Which of the following carbocations is more stable and why?



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.
- (b) (i) What is $\text{S}_{\text{N}}2$ mechanism? Give an example to explain it.
- (ii) Explain why *trans*-2-chlorocyclohexanol gives epoxy-cyclohexane 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.

2+3=5

1+1=2

3

1+1+3=5

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(4)

(d) Why is it difficult to separate racemic mixture? Describe a method of resolving a racemic mixture. $1\frac{1}{2}+3\frac{1}{2}=5$

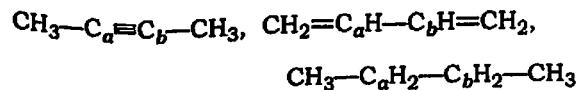
(e) What is atropisomerism? What types of isomerism are shown by 3-bromopent-2-ene? Give their structures along with their designation. Why are enantiomers not easily separated? $1+1+2+1=5$

4. Answer either (a) or (b), (c) or (d) and (e) or (f) from the following questions : $10\times 3=30$

(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



(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. $1+1+2=4$

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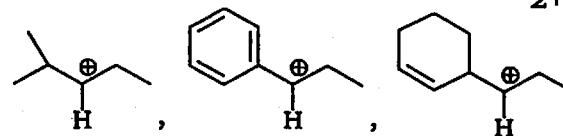
(5)

(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. 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

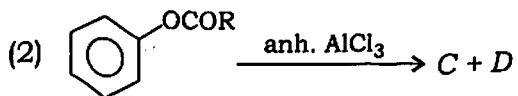
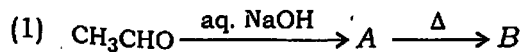
(d) (i) What are pyrolytic eliminations? Give an example. Propose a mechanism for the pyrolytic elimination reaction. $1+1+3=5$

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(6)

- (ii) Write a general mechanism for elimination reactions proceeding via the $E1$ 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 : $1 \times 2 = 2$



(7)

- (iii) Olefinic double bonds are prone to electrophilic addition whereas carbonyl $\text{C}=\text{O}$ bonds are prone to nucleophilic addition. Explain. 3
- (iv) Explain why elimination reactions always complete with substitution reaction. 3
