

2018

CHEMISTRY

(Major)

Paper : 1.2

(Organic Chemistry)

Full Marks : 60

Time : 3 hours

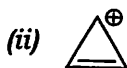
The figures in the margin indicate full marks for the questions

1. Answer the following questions (any seven) :

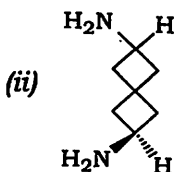
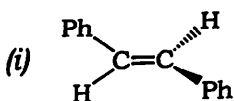
1×7=7

- (a) Draw the structural formula of bicyclo-[2, 2·2]octane.
- (b) Which of the following compounds has a longer C=C bond length?
 $\text{CH}_3\text{—CH=CH}_2$ and $\text{CH}_2\text{=CH}_2$
- (c) Give one example by which benzyne can be trapped.
- (d) Why is melting point of *p*-nitrophenol higher than *o*-nitrophenol?

(e) Classify the following as either aromatic, non-aromatic or anti-aromatic :



(f) Assign the absolute configuration *R/S* or *E/Z* to the following :



(g) Between ethanol and ethanethiol, which is stronger acid?

(h) Give one example of cross-conjugated compound.

2. Answer the following questions (any four) :

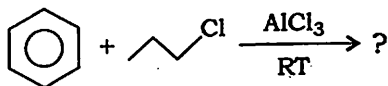
2×4=8

(a) What is S_Ni reaction? Write with an example.

(b) Write Fischer projection, staggered Sawhorse projection and Newman projection formulae of *threo*-2,3-dichloro-3-phenylpropanoic acid.

(c) Why is triplet carbene more stable than singlet carbene? Explain.

- (d) What is the major product of the following reaction? Justify your answer and give the name of the reaction :



- (e) Why does acid catalyzed dehydration of neopentyl alcohol yield 2-methyl-2-butene as the major product?

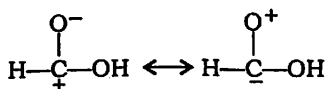
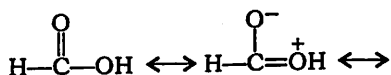
3. Answer the following questions (any three) :

5×3=15

- (a) Define dipole moment. How is it related to melting and boiling point? Why is dipole moment of nitrobenzene ($\mu = 3.95\text{D}$) higher than nitromethane ($\mu = 3.60\text{D}$) although both have same polar group? What is the μ -value of *p*-dinitrobenzene?

1+1+2+1=5

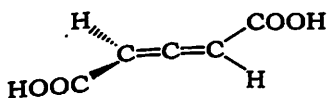
- (b) (i) Arrange the following resonating structures in the order of decreasing stability and give reasonable explanation : 1+2=3



(ii) Explain why 1,3,5-cycloheptatrienyl cation is aromatic but 1,3,5-cycloheptatriene is not. 2

(c) Give the evidences for the formation of σ - and π -complexes in electrophilic aromatic substitution. Write the mechanism for the nitration of benzene. 3+2=5

(d) (i) The allene



is optically active although it has no chiral centre. Explain. 2

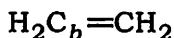
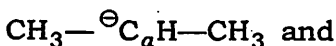
(ii) How is a racemic mixture different from *meso*-compound? Give examples to illustrate the differences. 2+1=3

(e) (i) What happens when pyridine is treated with NaNH_2 ? Give the mechanism. 2½

(ii) Write the mechanism of cyclopropanation of alkene with singlet carbene. 2½

4. Answer the following questions [either (a) or (b), (c) or (d) and (e) or (f)] : 10×3=30

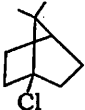
- (a) (i) What is trigonal hybridization? Write its characteristics. Find the types of hybridization of C_a and C_b in the following by electron pair method : 1+2+2=5



- (ii) What is *trans*-annular strain? The chair form of methylcyclohexane is less stable when methyl group is in axial position than it is in equatorial position. Explain. Draw the Newman projection for chair form of methyl cyclohexane when methyl group is (i) anti to C_3 and (ii) anti to C_5 . 1+2+2=5

Or

- (b) (i) What is S_N1 reaction? What are the evidences for S_N1 reactions? Why does >Br give S_N1 reaction

whereas  does not give S_N1 reaction? 1+2+2=5

- (ii) What do you mean by kinetically controlled and thermodynamically controlled reaction? Give two reactions to justify such reactions.

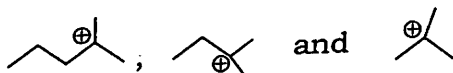
2+3=5

- (c) (i) The addition of HBr to propene is regioselective. Explain this statement and illustrate the steps involved in the mechanism of the reaction.

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- (ii) What is pK_a ? Between 2-bromopentanoic acid and 3-bromopentanoic acid, which one has higher pK_a value and why? 1+2=3

- (iii) What are carbanions? How are they different from carbene? Arrange the following carbocations in increasing order of their stabilities : 1+1+1=3

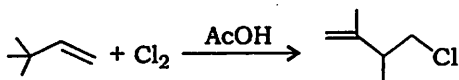


Or

- (d) (i) Why does ethoxymethylchloride react with nucleophiles 10^6 times faster than 1-chlorobutane even though both are primary alkyl chloride? Explain.

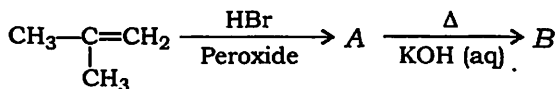
3

- (ii) Write the mechanism for the following conversion : 2



- (iii) 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. 2+3=5

- (e) (i) Draw and label the *E,Z*-isomers of 1,2-dichloro-3-ethyl-4-methyl-2-pentene. 1
- (ii) Write the structure of *meso*-tartaric acid. Is it optically active? Give the *R,S*-nomenclature for the two chiral centres in *meso*-tartaric acid. 1+1+1=3
- (iii) What are configurational and conformational isomers? Draw the possible conformations of *n*-butane. Arrange the conformations in order of decreasing stability. 2+2+1=5
- (iv) What are the products A and B in the following? 1



Or

- (f) (i) Under what conditions E2-elimination reaction is syn-elimination? Discuss a pyrolytic syn-elimination reaction with one example. 2+2=4
- (ii) Define carbon-free radicals. How can carbon-free radical be generated? 1+2=3
- (iii) Distinguish S_N1 reaction from S_N2 reaction. 3
