

2017

CHEMISTRY

(Major)

Paper : 1.2

(Organic Chemistry)

Full Marks : 60

Time : 3 hours

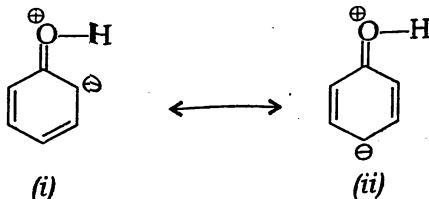
*The figures in the margin indicate full marks
for the questions*

1. Answer/Choose the correct option for the following (any seven) : 1×7=7

(a) Write the IUPAC name of the following compound :

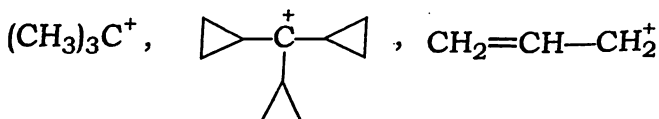


(b) Which of the following structures contributes more to its resonance hybrid?

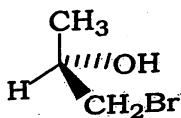


(2)

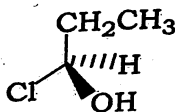
- (c) Why is the boiling point of ethyleneglycol much lower than that of glycerol?
- (d) Why is 1,3,5-cycloheptatrienyl cation aromatic but 1,3,5-cycloheptatriene is not?
- (e) Arrange the following carbocations in increasing order of their stability :



- (f) Between *o*-hydroxybenzoic acid and *p*-hydroxybenzoic acid, which is stronger acid and why?
- (g) Assign *R*- or *S*-configuration to each of the following compounds :



(i)



(ii)

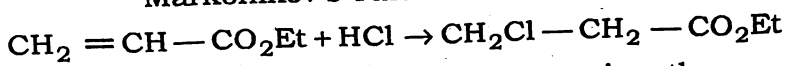
- (h) The number of optically active isomers of $\text{HOCH}_2(\text{CHOH})_4\text{CHO}$ is

- (i) 4
(ii) 8
(iii) 16
(iv) 24

2. Answer the following questions (any four) :

2×4=8

- (a) Explain that cyclopentadiene is acidic ($pK_a = 16$).
- (b) The chair conformation of cyclohexane is more stable than the boat conformation. Explain.
- (c) Why does the addition of HCl to the following olefin take place in the opposite manner as predicted by Markonikov's rule?



- (d) Benzylchloride is more reactive than alkylchloride in nucleophilic substitution reaction. Why?
- (e) Account for the fact that naphthalene is less aromatic than benzene.

3. Answer the following questions (any three) :

5×3=15

- (a) What are kinetic and thermodynamic products? Justify these by taking naphthalene as an example at different temperatures (80 °C and 160 °C). 2+3=5
- (b) What is stereocentre? Justify with an example that enantiomer has stereocentre. Draw all the possible geometrical isomers of 2,5-heptadiene.

1+2+2=5

(4)

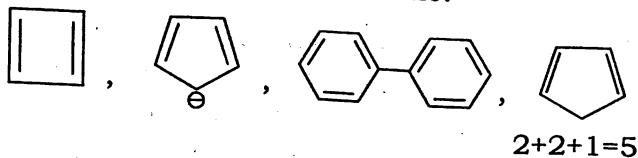
(c) What are different types of carbene? Distinguish between them. Give one method of formation of carbene. 1+2+2=5

(d) What are electrophiles? Why does electrophilic substitution to naphthalene preferably take place at α -position rather than β -position? Write one alkylation of naphthalene with mechanism. 1+2+2=5

(e) What is a *meso*-compound? How many different stereoisomers of tartaric acid are there? Give the *R*-, *S*-notations for the two chiral centres in *meso*-tartaric acid. 1+2+2=5

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

(a) (i) What are aromatic compounds? Classify the following molecules as aromatic, anti-aromatic or non-aromatic. Why is 1,3,5,7-cyclo-octatetraene not aromatic?

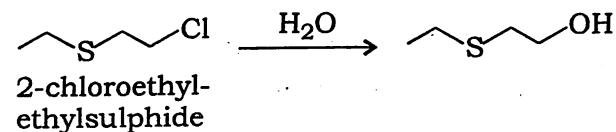
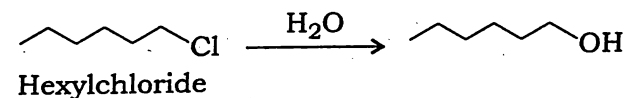


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(Continued)

(5)

(ii) What is anchimeric assistance? How does it affect the rate of a reaction? Write the mechanism for the following transformation and comment on the rate of the reaction : 1+2+2=5



Or

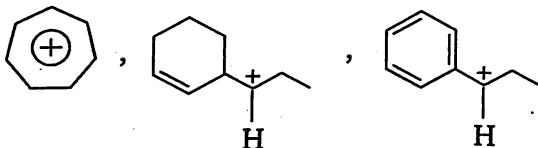
(b) (i) Why is maleic acid much stronger acid than fumaric acid even though they have same molecular formula, $\text{C}_4\text{O}_4\text{H}_4$? What kinds of stereomeric products are obtained when maleic and fumaric acids are treated with Br_2 in CCl_4 separately? Also mention the optical activity of the products. 2+3=5

(ii) Explain why elimination reactions always compete with substitution reaction. How can you convert butanol-1 to butene-1 by pyrolytic elimination? 3+2=5

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(Turn Over)

- (c) (i) What are carbocations? How can you generate carbocations? Arrange the following carbocations in decreasing order of stability and explain the reasons : 1+2+2=5



- (ii) Which one is more reactive towards nucleophiles—acetaldehyde or acetone? Explain. 3
- (iii) Addition of HCl to 1,3-butadiene gives both the 1,2- and 1,4-addition products. Using this example, explain kinetic and thermodynamic controls in reactions. 2

Or

- (d) (i) Between pyridine and piperidine, which one is a stronger base and why? 2
- (ii) Why does dibenzoyl methane not give addition compound with HCN even though there are two C=O groups? Explain. 2

(iii) Explain with examples that addition of singlet carbene to alkene is stereospecific whereas with triplet carbene it is not stereospecific.

3

(iv) Write all the possible chain isomers of the molecule having molecular formula, C_5H_{12} and give their IUPAC nomenclature. Arrange these isomers in decreasing order of their boiling point.

1+1+1=3

(e) (i) Acid-catalyzed dehydration of neopentyl alcohol yields 2-methyl-2-butene as the major product. Outline a mechanism showing all steps in its formation.

2

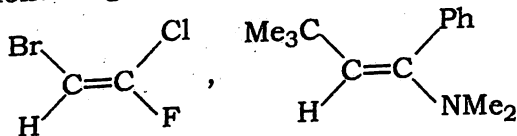
(ii) Why does alkyl fluoride give Hofmann elimination whereas alkyl iodide gives Saytzeff elimination?

2

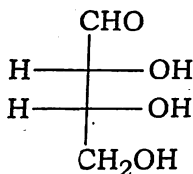
(iii) Why is it difficult to resolve a racemic mixture?

2

(iv) Assign *E*- or *Z*-nomenclature for the following molecules :

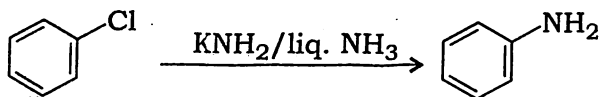
 $\frac{1}{2} + \frac{1}{2} = 1$ 

- (v) Convert the following molecule into sawhorse and Newman projections. Why is staggered form more stable than eclipsed form? 2+1=3



Or

- (f) (i) How is benzyne intermediate generated? Give the mechanism for the following transformation :



How can you trap benzyne intermediate? 1+2+1=4

- (ii) In the chair form of cyclohexylhalide, nucleophilic substitution by S_N2 process for axial substituent of halide is faster than that of an equatorial substituent of halide. Explain. 3
- (iii) Define enantiotopic and diastereotopic hydrogens and a prochirality centre. Illustrate your answer with suitable examples. 3
