

2014

CHEMISTRY

(Major)

Paper : 1.2

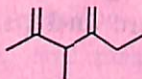
Full Marks : 60

Time : 2½ hours

The figures in the margin indicate full marks for the questions

1. Answer the following questions : 1×7=7

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



(b) Draw the structural formula of spiro [3.3] heptane-2-carboxylic acid.

(c) In which of the following two compounds C—O—C bond angle is greater and why?

Dimethyl ether and diphenyl ether

(d) What will happen when azides are photolytically decomposed? Write the reaction.

- (e) Though three-membered cyclic compounds are generally unstable, cyclopropanone is stable. Explain.
- (f) Arrange the following compounds in order of decreasing dipole moment :
p-chloronitrobenzene, nitrobenzene, chlorobenzene
- (g) Define specific rotation.

2. Answer the following questions (any four) :

- (a) Draw the tautomeric forms of nitromethane. Which form is more stable and why? 1+1
- (b) How is hydrogen bonding affected by (i) temperature and (ii) concentration? 1+1
- (c) Between *o*-chloroaniline and *p*-chloroaniline, which one is a weaker base and why? $\frac{1}{2}+1\frac{1}{2}$
- (d) Give the appropriate structures of—
 (i) *syn*-3,4-dibromohexane;
 (ii) *anti*-3,4-dibromohexane. 1+1
- (e) Distinguish between asymmetry and dissymmetry. 2

3. Answer the following questions : $5 \times 3 = 15$

(a) Explain why—

(i) pent-1-yne has lower pK_a than pent-1-ene;

(ii) salicylic acid has lower pK_a than *p*-hydroxybenzoic acid. $2+3$

Or

(b) Explain why—

(i) amides are protonated on oxygen rather than nitrogen;

(ii) $(CH_3)_3\overset{+}{N}CH_2COOH$ has lower pK_a than $(CH_3)_3CCH_2COOH$. $2\frac{1}{2}+2\frac{1}{2}$

(c) (i) Using aniline as an example, explain the meaning of resonance effect.

(ii) In picryl iodide, which C—N bond is longer and which is shorter? Provide an explanation. $2+1+2$

Or

(d) (i) The heat of hydrogenation of but-1-ene is $30.3 \text{ kcal mol}^{-1}$. What is your expectation regarding the heat of hydrogenation of buta-1,3-diene? Provide an explanation.

(ii) Draw the resonating structures of *N,N*-dimethyl formamide and comment on their relation stabilities. 3+2

(e) (i) What type of isomerism is shown by 3-bromopent-2-ene? Give their structures along with their designations. $\frac{1}{2}+2$

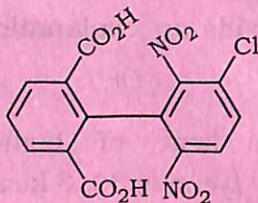
(ii) Between diastereomers and enantiomers which can be separated easily? Why? $\frac{1}{2}+1$

(iii) Define stereomutation. 1

4. Answer the following questions [Either (i) and (ii) or (iii) and (iv) from (a), (b) and (c)] :

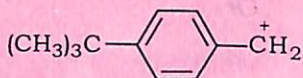
10×3=30

(a) (i) State giving reasons whether the following compound exhibits optical activity or not. If so, draw the enantiomers :



Give examples of σ -diastereomers. 3+2

- (ii) What are carbocations? Suggest one general method for its generation. What kind of structure simple alkyl carbocations generally adopt? Which one between the following two carbocations is more stable and why?



1+1+1+2

Or

- (iii) What are the different types of carbene? How can you distinguish between them? Give an example of a name reaction involving carbene as an intermediate.

1+3+1

- (iv) Why is it difficult to resolve a racemic mixture? Describe in detail a method for resolving a racemic mixture.

1+4

- (b) (i) Olefinic double bonds are prone to electrophilic additions whereas carbonyl bonds are prone to nucleophilic additions. Explain. Propose a general mechanism for nucleophilic addition of Grignard reagent to a carbonyl group.

3+2

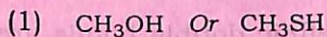
- (ii) Write a general mechanism for elimination reactions proceeding via the $E1$ pathway. Provide two evidences in support of the mechanism. 3+2

Or

- (iii) Hydroboration-oxidation reaction is an example of anti-Markownikoff addition. Explain with the help of an example and mechanism. 5

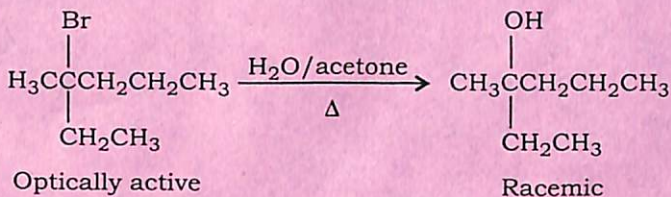
- (iv) "E2 reactions are stereospecific." Explain the statement. 5

- (c) (i) Distinguish between basicity and nucleophilicity. Indicate which reagent in each pair is expected to be more nucleophilic toward CH_3Br in ethanol and why.

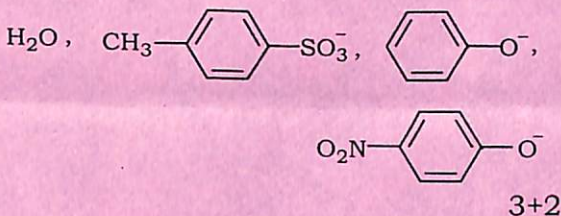


(7)

- (ii) Account for the stereochemical course of the following reaction :



Arrange each of the following sets of ions in decreasing order as leaving groups in nucleophilic substitution :



Or

- (iii) What do you mean by pyrolytic eliminations? Give an example of a pyrolytic elimination reaction. Propose a mechanism for the reaction. 1+1+3
- (iv) What factors can be used to determine whether an aliphatic nucleophilic substitution proceeds by the $\text{S}_{\text{N}}1$ or $\text{S}_{\text{N}}2$ mechanism? Explain two of the factors in brief. 1+4
