PB-163

M.Sc. Chemistry (1st Semester)
Examination, Dec., 2018

Paper - II

Organic Chemistry, Stereo-Chemistry and Pericyclic Reactions

Time : Three Hours] [*Maximum Marks* : 80
[*Minimum Pass Marks* : 29

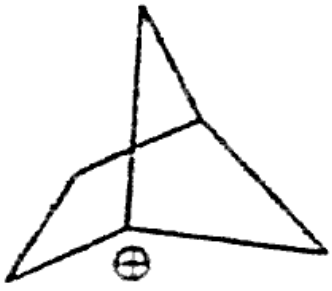
Note : Answer from **both** the Sections as directed. The figures in the right-hand margin indicate marks.

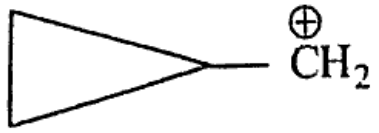
SECTION-A

1. Answer the following questions in brief : 1×10

(*a*) Which of the following is bridge head carbocation ?

(*i*) $C_6H_5-\overset{\oplus}{C}H_2$

(*ii*) 

(*iii*) 

(*iv*) $H_2C=CH-\overset{\oplus}{C}H_2$

(*b*) Define Hyperconjugation.

(*c*) Write the name and structure of one optical active compond which has no chiral carbon atom.

(*d*) Write the conformation of α-D-mannose.

(*e*) Give one example of cheletropic reaction.

(*f*) What is the difference between intermediates and transition states.

(*g*) Pentadienyl anion + ethylene → cyclo-heptenyl anion. Determine whether the above reaction is symmetry allowed thermally or photochemically.

(*h*) What is sigmatropic rearrangement ?

(*i*) Write Shapiro reaction.

(*j*) Give one example of molecular rearrangement which occur due to the rearrangement of electron deficient oxygen.

2. Answer the following questions in concise manner : 2×5

(*a*) Define homoaromaticity and antiaromaticity.

(*b*) What is the difference between conformation and configuration ?

(*c*) Define the term isotope labelling with example.

(*d*) What is Cope-rearrangement ?

(*e*) What do you understand by migratory aptitude and memory effect ?

SECTION-B

Answer **all** questions :

Unit-I

3. (*a*) What are alternate and non-alternate hydrocarbons ? Explain in detail with suitable example. 6

(*b*) What is singlet and triplet state of carbene ? How will you convert benzene into cyclohepta triene ester with the use of carbene ? 6

OR

(*a*) Explain the acidic nature of phenol on the basis of resonance. 2

(*b*) What are Fullerenes ? Explain the bonding in Fullerenes. 2

(*c*) Discuss the aromaticity of (10) annules, (12) annulenes, (16) annulenes and (18) annulenes. 8

Unit-II

4. (*a*) Discuss the method for resolution of racemic mixture in optically active compounds. 6

(*b*) What is asymmetric synthesis ? Describe with using suitable examples. 6

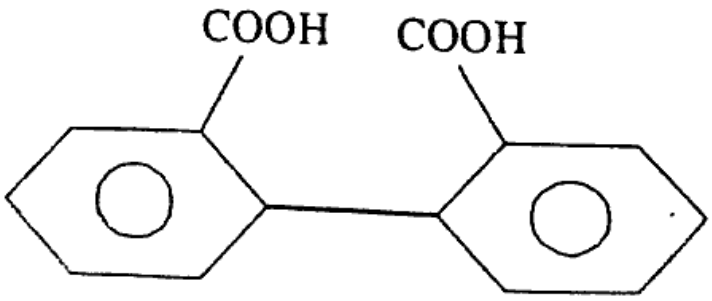
OR

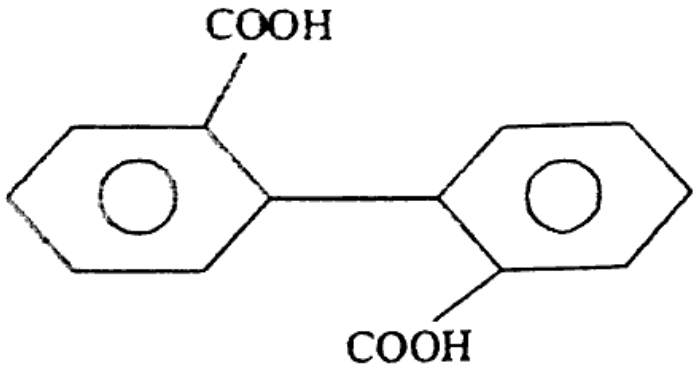
(*a*) Explain the following terms with suitable example. 6

(*i*) Optical purity

(*ii*) Enantiotropic and diastereotropic atoms, groups and faces.

(*b*) Discuss the elements of symmetry in detail. What type of symmetry is there in the following structures ? 6





Unit-III

5. (*a*) Explain in detail Hammett equation and its modification. Explain the significance of substituent constant (σ) and the reaction constant (ρ). 6

(*b*) Draw the energy profile diagram for the following reactions and explain the reaction : 6

(*i*) A one step reaction

(*ii*) A two step reaction in which the second step is rate determining.

OR

(*a*) What is Isotope effect ? Explain the use of isotope effect in ascertaining the mechanism of a reaction. 6

(*b*) Explain the following : 6

(*i*) Thermodynamic requirements for reaction

(*ii*) Kinetic requirements for reaction

Unit-IV

6. (*a*) Explain Woodward-Hoffmann selection rules for thermal and photochemical reactions with the help of correlation diagram and suitable example. 8

(*b*) Explain 1, 3 sigmatropic rearrangement. Why concerted 1, 3 sigmatropic shift of hydrogen is thermally forbidden ? 4

OR

(*a*) What is Ene reaction ? Explain its mechanism. 3

(*b*) Explain with example antarafacial and suprafacial addition. 3

(*c*) Why Diel's Alder reaction is thermally allowed process ? Explain with the help of correlation diagram and FMO method. 6

Unit-V

7. (*a*) Discuss Favorskii rearrangement under the following heads : 8

(*i*) Definition with reactions

(*ii*) Reagents

(*iii*) Mechanism

(*iv*) Application

(*b*) What do you understand by migratory aptitude and memory effect ? 4

OR

(Continued)

(*a*) Explain Baeyer-Villiger oxidation under the following heads : 8

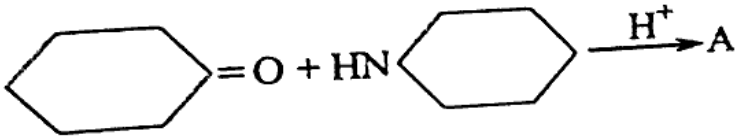
(*i*) Definition with examples

(*ii*) Reagents

(*iii*) Mechanism of the reaction

(*iv*) Application

(*b*) Identify the compound A and B and name the reaction in the following reactions : 4

(*i*) 

(*ii*) $\begin{matrix} R \\ R \end{matrix} > C = 0 \xrightarrow{RICO_3H} B$