## PG CBCS

M.SC. Semester-III Examination, 2021

## CHEMISTRY

PAPER: CEM 302
(ORGANIC SPECIAL )

## Answer any FOUR questions from the following:

1. Write down the Woodward-Hoffmann selection rules for H -and C -migration in sigmatropic reaction. Draw the pi-molecular orbital diagram of cyclopentadienyl radical indicating symmetry of molecular orbitals, electron occupancy, node of molecular orbital wave functions, SOMO and LUMO and explain the feasibility of [1,5] hydrogen shift of cyclopentadinene system in thermal condition using the above pi-molecular orbital. Define supra and antara facial processes in sigmatropic reactions.
2. (a) Write short notes on any two of the following the following:
(i) Ene reaction (ii) Claisen rearrangement (iii) Oxy-cope rearrangement
(b) Explain selective formation of products in the following electrocyclic reactions:



3. Suggest mechanism for following pericyclic reactions:
(a)

(b)


(d)

4. (a) Describe oxidative addition and reductive elimination reaction in organometallic compounds.
(b) Give the products of following reactions:

(c) Why ferrocene is more stable than cobaltocene?
5. (a) Write short note on the following:
(i) Wilkinson Catalyst (ii) Fluxional molecule
(b) Propose mechanism for the following reactions. The first step of which is catalytic.

B.

6. (a) Write the product and suggest the mechanism of following reactions:
(i)

(ii)

(b) Why TMEDA (tetra methyl ethylene diamine) is required for dilithiation of ferrocene? 2
(a) Suggest mechanism of following reactions:
(i)

(ii)

(iii)

(b) What is the oxidation state of iron in ferrocene?
7. (a) Draw the molecular orbital diagram of ferrocene.
(b) Define sigmatropic shift of order [i,j] with an example. Show that [1,5]-H suprafacial shift is allowed by the Woodward-Hoffmann rule for thermal pericyclic reactions with the help of Frontier molecular orbital diagram.
8. Derive the Hammett equation (LFER). What are reaction constant and substituent constant?
$6+2+2$

## (4)

10. (a) The $\rho$ value for the benzoylation of $m$ - and $p$-substituted anilines is -2.69 and $\rho$ value for base catalysed hydrolysis of $m$ - and $p$-substituted ethyl benzoates is +2.51 . Explain its significance. $3+3$
(b) Describe the Taft modification of Hammett equation. What is Yukawa-Tsuno equation?
