PG CBCS

M.SC. Semester-III Examination, 2021 **CHEMISTRY**

PAPER: CEM 302

(ORGANIC SPECIAL)

Full Marks: 40 **Time: 2 Hours**

Answer any FOUR questions from the following:

4 X 10=40

- 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. 4+4+2
- 2. (a) Write short notes on *any two* of the following the following:

6

- (i) Ene reaction (ii) Claisen rearrangement (iii) Oxy-cope rearrangement
- (b) Explain selective formation of products in the following electrocyclic reactions:

4

3+3+4

3. Suggest mechanism for following pericyclic reactions:

2.5x4

(b)

(P.T.O.)

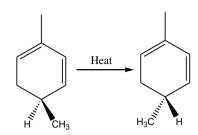
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1

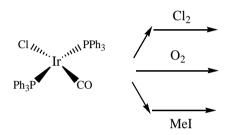
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(2)

(d)



- 4. (a) Describe oxidative addition and reductive elimination reaction in organometallic compounds. 3+3
 - (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.

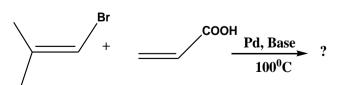
A.
$$\begin{array}{c} Pd(PPh_3)_4 \\ PPh_3 \end{array}$$

$$\begin{array}{c} O \\ PhCH_2NH_2 \end{array} + \begin{array}{c} O \\ O \\ \hline O \end{array}$$

$$\begin{array}{c} O \\ O \\ \hline O \end{array}$$

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

(i)



4

4x2

(b) Why TMEDA (tetra methyl ethylene diamine) is required for dilithiation of ferrocene? 2

(a) Suggest mechanism of following reactions:

3x3

(i)

(ii)

(iii)

(b) What is the oxidation state of iron in ferrocene?

1

8. (a) Draw the molecular orbital diagram of ferrocene.

6

- (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.
- 9. Derive the Hammett equation (LFER). What are reaction constant and substituent constant?

6+2+2

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

2+2