

PG CBCS
M.Sc. Semester-III Examination, 2022
CHEMISTRY
 PAPER: CEM-302

(ADVANCED ORGANIC CHEMISTRY-I (ORGANIC SPL.))

Full Marks: 40

Time: 2 Hours



GROUP - A

1. Answer any **FOUR** questions from the following questions: 2×4 = 8

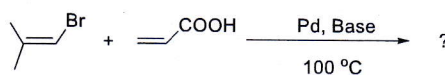
- a) What do you mean by reaction constant (r) in Hammett equation?
- b) How is the substituent constant (σ_x) defined?
- c) Compare the Hammett plots of hydrolysis of ArCO_2Me and ArCO_2Et .
- d) Why TMEDA (tetra methyl ethylene diamine) is required for di-lithiation of ferrocene?
- e) What is the oxidation state of iron in ferrocene? Explain on the basis of 18 electron rule.
- f) Define torquo- and peri-selectivity with examples.
- g) Define supra and antara facial processes in sigmatropic reactions.
- h) Predict the hapticity of each Cp ring in $\text{Cp}_2\text{W}(\text{CO})_2$, and of each "triphos" in $[\text{Pd}\{(\text{PPh}_2\text{CH}_2\text{CH}_2)_3\text{CPh}\}_2]^{2+}$

GROUP - B

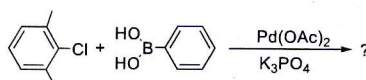
2. Answer any **FOUR** questions from the following questions: 4×4 = 16

- a) Write the product(s) and suggest the mechanism of each of following reactions

(i)

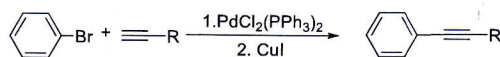


(ii)

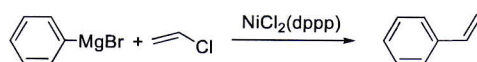


- b) Suggest mechanism of the following reactions:

(i)



(ii)



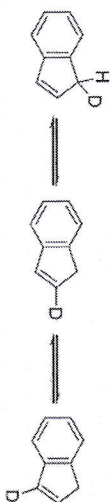
(1)

(P.T.O.)

- c) Derive the Hammett equation (LFER). What is Yukawa-Tsuno equation?
 d) Suggest mechanism for the following pericyclic reactions:
 (i)

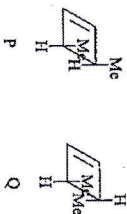


(ii)

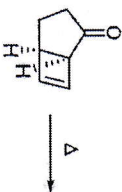


- e) (i) Reductive eliminations can sometimes be encouraged to take place by oxidizing the metal. Why do you think this is so?
 (ii) Water has two lone pairs. Decide whether both or only one of these should normally be counted, given that the following typical complexes exist:
 $[\text{IrH}_2(\text{PPh}_3)_2(\text{OH}_2)_2]^+$, $[\text{Os}(\eta^6\text{-C}_6\text{H}_6)(\text{OH}_2)_3]^2+$
 f) 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.
 g) Write short notes on *any two* of the following:
 (i) Claisen rearrangement (ii) Oxy-scope rearrangement (iii) Still coupling reaction (iv) Oxidative addition reaction.

- h) (i) Which of the following compounds will have a lower activation energy for the thermal ring opening reaction?



(ii) Predict the product of the following reaction and explain.



(2)

(P.T.O.)

GROUP - C

3. Answer any TWO questions from the following questions: 8x2 = 16

- a) Write down the Woodward-Hoffmann selection rules for H-band C-migration in sigma-tropic 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 cyclopentadiene system under thermal condition using the above pi-molecular orbitals. 4+4

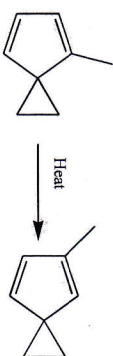
- b) Suggest mechanism of the following reactions: 4 x 2



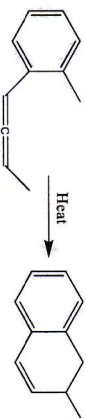
(ii)



(iii)



(iv)



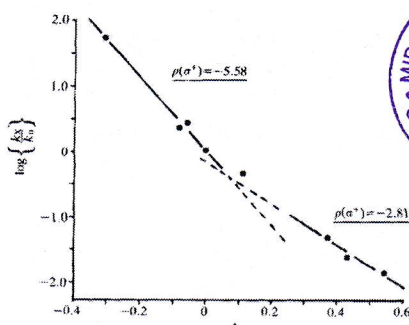
- c) Write short notes on the following 2 x 4

- (i) Ene reaction, (ii) Chelotropic reaction, (iii) Suzuki reaction, (iv) Heck reaction.

(3)

(P.T.O.)

- d) (i) For the following Hammett plot and reaction below, two reactions (susceptibility) constants (ρ) are obtained, one for EDG and another for EWGs. Explain the magnitude and sign of each of the two reaction constants and provide mechanism/s consistent with these observations.



- (ii) Why are *ortho*-substituents normally excluded from Hammett relationships?
 (iii) Discuss the possible causes for non-linear Hammett plots. (4 + 2 + 2)
