Birla Institute of Technology & Science, Pilani, Rajasthan - 333 031 Mid-semester Examination, 1st Semester 2022-2023

Course: CHEM F212 Course Title: Organic Chemistry-1 Time: 90 min. October 31, 2022 Max. Marks: 60

Instruction to students: Closed book, answer all questions and answer all parts of a question together.

Name: ID:

Q1. (a) Write structure of possible product(s) formed on reacting 1-cyclopentylethanol with HCl. 3.0

(b) The major product obtained from the following two reaction is identical. Write structure of the major product and explain the reason for selectivity in each case.

4.0

Q2. Using curved arrows write probable mechanism for the following transformations. 8.0

a)
$$AcOH$$
 AcO AcO

Q3. (a) Calculate substituent constant σ for NO₂ group given that pKa for p-nitrobenzoic acid and benzoic acid are 3.4 and 4.2, respectively.
2.0

(b) Consider the reaction below with $\rho = -1.32$. Based on Hammett equation, discuss whether the rate of the reaction will be suppressed or enhanced when X = Br is replaced with CN [Given that $\sigma(p-Br) = +0.23$ and $\sigma(p-CN) +0.66$]. Provide an explanation for your answer.

(c) If reactions to form A₂ and B₂ form A and B are exergonic and endergonic respectively, then

(i) the distance between two A's in the transition state would be relatively than the A-A bond in A_2 .

(ii) the transition state for the reaction of B_2 will resemble with the 2.0

Q4. (a) An optically active product is obtained when optically pure (1-bromoethyl)-benzene (A) is reacted with CH₃SNa in DMF. Based on the information, predict mechanism of the reaction and write structure of the product with appropriate stereochemistry (if any). What would be effect on product stereochemistry if the solvent is changed from DMF to methanol?

(A)

(b) We have studied that replacing an atom by a heavier isotope reduces the rate constant of the reaction. Extend this idea to rationalize isotope effects from a thermodynamic point of view and predict which acid HA or DA would be weaker?

2.0

In H_2O : $HA(aq) \stackrel{\leftarrow}{\rightarrow} H^+(aq) + A^-(aq)$

In D_2O : $DA(aq) = D^+(aq) + A^-(aq)$

(c) Propose an experiment with suitable substrate to demonstrate that the Fries rearrangement (shown below) is an intermolecular reaction.

3.0

(d) Which among methyl carbanion and trifluoromethyl carbanion has higher barrier to inversion and why?

3.0

Q5 Write structure of the product(s) for the following transformations.

12.0

f)
$$CH_3CO_2K$$
 CH_3CO_2H

(It is observed that rate of reaction depends on the concentration of both alkyl halide and base)

h)
$$+ CH_2N_2 \xrightarrow{Pd(OAc)_2}$$
 Ether

Q6 Suggest suitable reaction conditions including nucleophiles, solvents and temperature to obtain desired product from the compound X. 6.0

Q7 Propose a synthesis of each of the following compounds, from the given starting material and any other needed reagents (Not more than 7 steps).9.0

a)
$$\bigcap_{CN}$$
 \bigcap_{CN} \bigcap_{CN}

END