Birla Institute of Technology & Science, Pilani, Rajasthan - 333 031 Ist Semester 2017-2018 CHEM F212 ORGANIC CHEMISTRY I Mid Term Examination (Closed Book)

Duration: 90 minutes

Date: 12th October 2017

[2+2+3+3=10]

Write your name and ID no on the question papers. All questions are compulsory.

Max. Marks: 60

Q. No. 01. Propose a detailed mechanism for the following chemical transformations:



Q.No. 02. Identify the major product & propose a detailed mechanism for its formation:

[4+3+3=10]



Q.No. 03. (i) Consider the conversion of X to Y *via* a one-step mechanism. The activation energy of this conversion is 3 kcal/mol. The energy difference between B and the transition state of the reaction is 7 kcal/mol. Draw the energy profile diagram from the given information and estimate the ΔH_0 for the reaction X ----> Y. [1+1]

(ii) The value of reaction constant (ρ) for alkaline hydrolysis of methyl esters of substituted benzoic acids is 2.38. The rate constant for alkaline hydrolysis of methyl benzoate under similar conditions is $2x10^{-4}$ M⁻¹s⁻¹. Calculate the rate constant for hydrolysis of methyl *m*-nitrobenzoate, if σ (*m*-NO₂) = 0.71. Can you infer the structure of transition state/intermediate from the given information. [2+2]

(iii) cis 1-Chloro-2-methylcyclohexane yields a major trisubstituted alkene under E2 elimination conditions, while trans 1-chloro-2-methylcyclohexane yields a major disubstituted alkene under similar conditions. Identify the products and provide a reasoning. [1+1+2]

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Q.No. 04. (i) In the reaction profile below (left figure), which of the labels **A**, **B**, **C**, **D**, **E**, **F**, **G**, **H** correspond to the kinetically controlled product, the thermodynamic stable product, intermediate(s), and transition state(s) ?

[1+1+1+1]

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(ii) Consider the following reaction that could proceed either following path a or path b (right figure). The kinetics labeling studies when carried using a ¹⁴C isotope at the marked carbon (*) showed k (¹²C)/k (¹⁴C) = 1.072. Based on the information provided, indicate the preferred path of mechanism and justify your answer. [1+1]



(iii) Use the Hammond Postulate to explain why free radical bromination is more selective than free radical chlorination using an appropriate example. [4]

Q.No. 05. (i) Rank the following compounds from fastest to slowest as they react with $Br_2/FeBr_3$. [2] [*Answer like: fastest* ... > ... > ... > ... > ... > ... > ... > ... slowest]

