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EASETRN UNIVERSITY, SRI LANKA

SECOND EXAMINATION IN SCIENCE 2013/2014

SENCOND SEMESTER

CH 104: ORGANIC REACTION MECHANISMS . . .

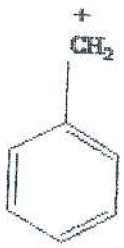
(Proper)

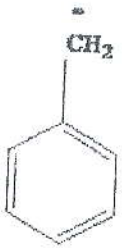
Answer all questions

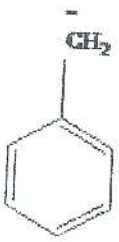
Time: One hour

1.

a) Draw the resonance structures for the followings.

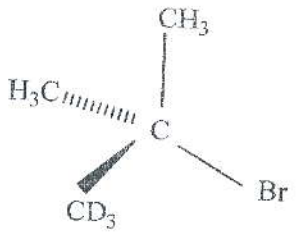
i. 

ii. 

iii. 

(30 Marks)

b) The compound **A** is treated with an aqueous solution of sodium hydroxide and this reaction gave **B** ($C_4H_7D_3O$) as the product. The rate of this reaction was found to depend **only** on the concentration of the compound **A**.



Compound A

(i). Give the structure (including the stereochemistry) of the product **B**

(ii). Write down the mechanism involved in the formation of **B** from **A**.

(iii). Draw a fully labelled energy profile diagram for the above reaction and clearly indicate the reactants, transition state(s), intermediate(s) and products.

(50 Marks)

c) Briefly explain why alcohols are less acidic than carboxylic acids.

(20 Marks)

2) a) A reaction follows first order kinetics,

i) Show that the integrated form of the rate equation is given by

$$kt = \ln\left(\frac{c_0}{c_0 - x}\right)$$

where c_0 , k and x denote the initial reactant concentration, the first order rate constant, and the concentration reacted at time t respectively.

ii) If y denotes the fraction of reactant reacted at time t, show that

$$kt = \ln\left(\frac{1}{1 - y}\right)$$

iii) Derive an expression for the half-life of a first order reaction and use this expression to show that in a first order reaction the time taken for the reactant concentration to drop by 3/4 of its initial value is doubled the initial concentration to drop by 1/2 of its initial value.

(50 marks)

b) i) What is steady state approximation in chemical kinetics? Under what conditions will the steady state approximation be valid?

ii) Consider the following reaction mechanism:

$$CH_3CHO \xrightarrow{k_1} CH_3 + CHO$$

$$CH_3 + CH_3CHO \xrightarrow{k_2} CH_4 + CH_3CO$$

$$CH_3CO \xrightarrow{k_3} CH_3 + CO$$

$$CH_3CO + CH_3CO \xrightarrow{k_4} CH_3COCOCH_3$$

I) Identify the intermediates involved in the reaction.

II) Write the rate laws for the formation of CO, CH_3, and CH_3CO.

III) By assuming a steady state approximation for the intermediates, show that the rate of formation of CO:

$$\frac{d[CO]}{dt} = k_3 \left(\frac{k_1}{k_4}\right)^{1/2} [CH_3CHO]^{1/2}$$

(50 marks)

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