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14 (CHM-I) 102

2018

CHEMISTRY

Paper : CH 102

(Organic Chemistry)

Full Marks : 60

Time : Three hours

***The figures in the margin indicate
full marks for the questions.***

1. Answer **any four** questions : $4 \times 4 = 16$

(a) Give reasons why :

- (i) the ether bonds in epoxides can be cleaved for more easily than in open chains.
- (ii) though oxidation reaction to remove hydrogen from carbon atom normally requires harsh reaction condition, oxidation of dihydropyridine to pyridine removing hydrogen from carbon takes place easily under mild oxidation reaction condition.

Contd.

- (iii) While methyl esters are easily hydrolysed, *t*-butyl esters are extremely difficult to hydrolyze under basic conditions. 1+1+2

(b) For the following reaction system:



the rate of interconversion between A and B is much faster than the rate of conversion to C and D. Under these circumstances what determines the relative concentration of C and D in the product mixture?

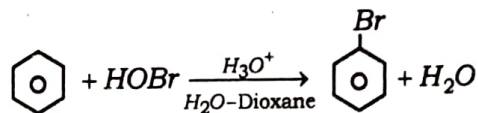
State and name the relevant principle and draw the reaction profile diagram illustrating the principle.

Explain the selective formation of trans-but-2-ene from base induced dehydrobromination of 2-bromobutane, on the basis of its conformational structures. 2+2

(c) What is Primary Kinetic Isotope Effect (PKIE)?

Explain why for dehydroiodination from ethyl iodide in presence of a strong base, the reaction has a large PKIE value.

The rate and PKIE results of the aromatic electrophilic substitution reactions are given below:



$$\text{Rate} = K [\text{HOBr}][\text{C}_6\text{H}_6][\text{H}_3\text{O}^+]$$

$$\text{and } \frac{K_{\text{C}_6\text{H}_6}}{K_{\text{C}_6\text{D}_6}} = 1$$

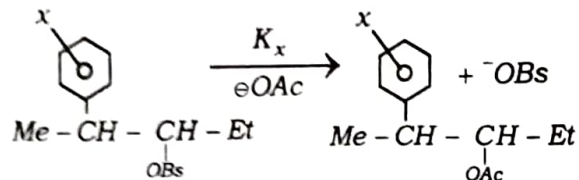
Suggest a mechanism for the reaction. 1+1+2

(d) What are σ and σ^* in Hammett and Taft equation?

The ρ value of alkaline hydrolysis of methyl esters of substituted benzoic acids is 2.38 and the rate constant for the alkaline hydrolysis of methyl benzoate under similar condition is $2 \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$. What will be rate const. for the hydrolysis of methyl-*m*-nitrobenzoate?

$$(\sigma_{m-\text{NO}_2} = 0.70) \quad 2+2$$

(e) For the following reaction :



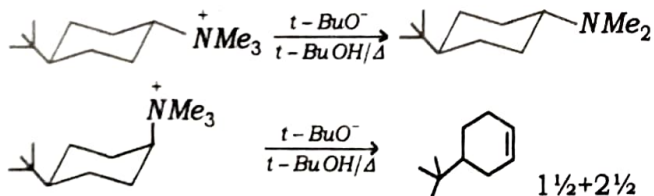
Bs = brosylate

The ρ value is -1.46 . When the substituents (X) were varied from strongly electron withdrawing ($-\text{NO}_2$) groups to electron donating groups ($-\text{OMe}$), through the weakly electron withdrawing groups, the Hammett plot gives a concave upward deviation. Explain the phenomenon in detail.

4

(f) What are stereoelectronic effects? State the main stereoelectronic rule.

Explain the products formed in the following reactions on the basis of stereoelectronic interactions.



$1\frac{1}{2} + 2\frac{1}{2}$

2. Answer **any four** questions : $4 \times 4 = 16$

(a) Examine the factors that help the stabilization of carbanions with suitable examples.

4

(b) Pick the correct choice and provide brief justification for each.

2+2

(i) Which of the following carbocations is most stable?

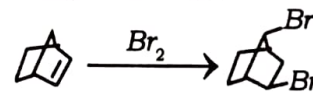


(ii) Which of the following compounds contain the most acidic C-H group (i.e. easily deprotonated) :



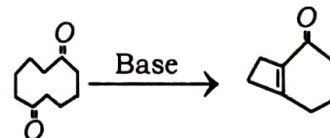
(c) Give the mechanistic pathway for the following reactions :

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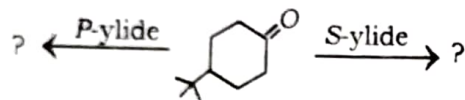


(d) Provide a mechanistic rationale for the following transformation :

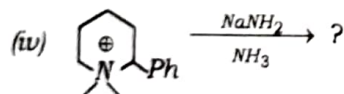
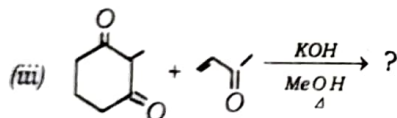
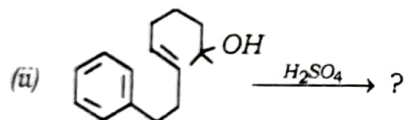
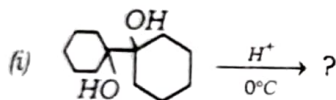
4



- (e) Comment on the stability of *P*-ylides. Taking an appropriate example of *P*= and *S*-ylide, explain the following reactions : 1+3



- (f) Complete any two of the following reactions : 2+2



3. Answer question (a) and **any three** from the rest. 2+3×4=14

- (a) Give two reactions showing formation of carbene. 2

- (b) Discussing the structures of singlet and triplet carbenes, explain why one is more reactive than the other. 4

- (c) Discuss the stereochemical outcome of addition reactions of carbenes to olefinic bonds, with illustrative examples. 4

- (d) What is Tebbe reagent and discuss its use in olefination? 1+3

- (e) What is Barton decarboxylation reaction? Discuss its mechanism. 1+3

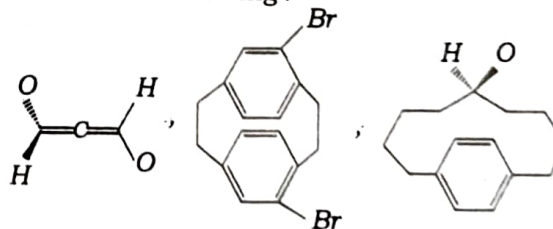
- (f) What is McMurry coupling? Discussing its mechanism identify its merits and demerits. 1+3

4. Answer (a) and **any two** from the rest :

6×2×4=14

- (a) Answer **any three** of the following :

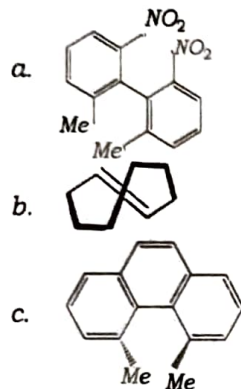
- (i) Identify the chiral compounds and the reason of chirality, among the following :



(ii) Match the contents of column I with that of column II :

Column I

Column II



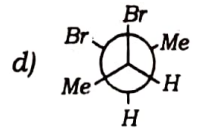
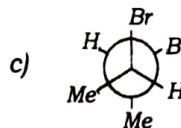
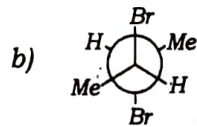
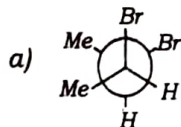
i. Chiral centre

ii. Chiral axis

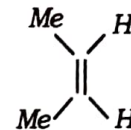
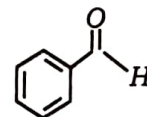
iii. Chiral plane

iv. Helical chirality

(iii) The gauche interaction values for Me/Me, Me/Br and Br/Br are 3.3, 0.8 and 3.0 kJ/mol. respectively. Identify the most stable conformation of 2,3-dibromobutane from amongst the following :



(iv) Designate the configuration of each face of the following two molecules in Re and Si system. $2 \times 3 = 6$



(b) Discuss the different classes of racemic modifications. What are quasiracemates? Explain your answer with suitable examples. 4

(c) In cyclobutanone (assuming planar structure) there are homotopic, constitutionally heterotopic and enantiotopic (stereoheterotopic) pairs of hydrogen atoms. Identify them with appropriate diagrams and explanations. 4

(d) Write the mechanism of ring inversion for cyclohexane molecule. Also draw the energy profile for various intermediates during of ring inversion. 4
