

BIRLA INSTITUTE OF TECHNOLOGY, MESRA, RANCHI
(END SEMESTER EXAMINATION)

CLASS: ISc/MSc
BRANCH: CHEMISTRY

SEMESTER : VII/I
SESSION : MO/2025

SUBJECT: CH405R1, PRINCIPLES OF ORGANIC SYNTHESIS

TIME: 3 Hours

FULL MARKS: 50

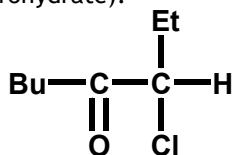
INSTRUCTIONS:

1. The question paper contains 5 questions each of 10 marks and total 50 marks.
2. Attempt all questions.
3. The missing data, if any, may be assumed suitably.
4. Before attempting the question paper, be sure that you have got the correct question paper.
5. Tables/Data hand book/Graph paper etc. to be supplied to the candidates in the examination hall.

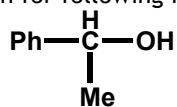
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|--|---------|----|-----|
| <p>Q.1(a) (i) When <i>trans</i>-2-methylcyclohexanol is treated with <i>p</i>-toluenesulphonyl chloride followed by KOEt, 3-methylcyclohexane is the only product. On the other hand, <i>cis</i>-2-methylcyclohexanol under same condition gives 1-methylcyclohexane as the main product. Account for the differences.</p> <p>(ii) Ethyl <i>trans</i>-4-<i>t</i>-butyl cyclohexane carboxylate undergoes base catalysed hydrolysis twenty times faster than its <i>cis</i>- isomer.</p> <p>(iii) Both <i>cis</i>- and <i>trans</i> -4-hydroxycyclohexanecarboxylic acids are separately heated. Indicate the structural changes, if any.</p> | [2x3] | 1 | I |
| <p>Q.1(b) (i) Explain why the <i>trans</i>-2-acetoxycyclohexyl tosylate undergoes acetolysis 670 times faster than the corresponding reaction of <i>cis</i>-2-acetoxycyclohexyl tosylate and that the product has the same <i>cis</i>-stereochemistry in both the cases.</p> <p>(ii) <i>Cis</i>- form of 1,2-dimethylcyclohexane exists as a pair of conformational enantiomers and it is difficult to separate them, explain. Under which condition can their inter-conversion be stopped?</p> | [2x2] | 2 | II |
| <p>Q.2(a) From the cross experiment establish the mechanism of Claisen rearrangement. Established the mechanism for following reaction from the information about the products formed.</p> <div style="text-align: center; margin: 10px 0;"> </div> | [3+2] | 2 | II |
| <p>Q.2(b) What is inverse kinetic isotope effect? Discuss the difference between primary and secondary kinetic isotope effect. Explain the type of kinetic isotope effect shown by the following reaction.</p> <div style="text-align: center; margin: 10px 0;"> </div> | [1+2+2] | 2 | III |
| <p>Q.3(a) Derived simplified equation based on Curtin-Hammett principle with proper energy profile diagram:</p> <div style="text-align: center; margin: 10px 0;"> $C \xleftarrow{k_1} A \xrightleftharpoons{K} B \xrightarrow{k_2} D$ </div> | [4] | 3 | I |
| <p>Q.3(b) Give examples with mechanism in each case:</p> <ol style="list-style-type: none"> (i) More stable conformers react more quickly. (ii) Less stable conformers react more quickly. (iii) both conformers react at the same rate. | [2x3] | 3 | II |

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- Q.4(a) Predict and explain the minor and major products for the reduction of following compound by NaBH₄ (sodium borohydrate). [2x2.5] 3 IV

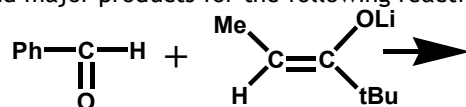


Describe the principle of resolution for following racemic mixture.

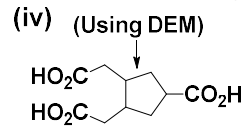
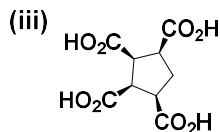
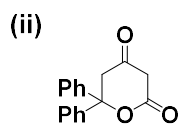
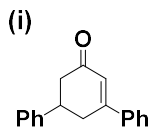


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- Q.4(b) Give the example for the use of chiral reagent for MPV reduction. Predict and explain the minor and major products for the following reaction. [2+3] 4 IV



- Q.5 Give retrosynthetic analysis and an efficient synthesis of each of the following. [2.5x4] 4 II



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