LOYOLA COLLEGE (AUTONOMOUS) CHENNAI – 600 034

M.Sc. DEGREE EXAMINATION – **CHEMISTRY**

FIRST SEMESTER – **NOVEMBER 2024**

PCH1MC01 – ORGANIC REACTION MECHANISM AND STEREOCHEMISTRY

Date: 08-11-2024 Dept. No. ☐ Max. : 100 Marks
Time: 01:00 pm-04:00 pm

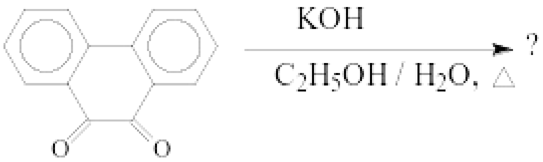
SECTION A – K1 (CO1)

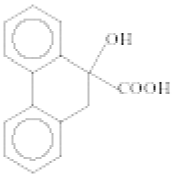
Answer ALL the questions **(5 x 1 = 5)**

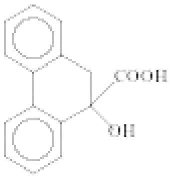
1 MCQ

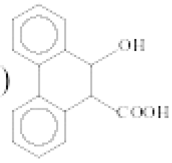
a) Which of the following statements is incorrect?
(i) Chlorination of an alkane is an exothermic reaction.
(ii) Early transition state resembles the geometry of the reactants.
(iii) Nitration of benzene does not follow microscopic reversibility.
(iv) Chlorination of toluene in $AlCl_3$ gives benzyl chloride.

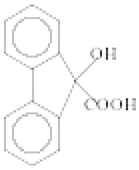
b) The product obtained by the following reaction is



(i) 

(ii) 

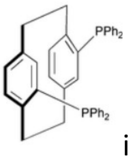
(iii) 

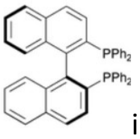
(iv) 

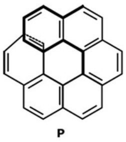
c) Which of the following order is correct with LAH as reducing agent?
(i) Ester > amide > carboxylic acid > ketone > aldehyde
(ii) Carboxylic acid > amide > ester > ketone > aldehyde
(iii) Aldehyde > ketone > ester > amide > carboxylic acid
(iv) Aldehyde < ketone < ester < amide < carboxylic acid

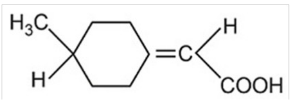
d) Identify the incorrect statement
(i) Stereoisomers have same connectivity but differ in the arrangement of their atoms in space.
(ii) Constitutional isomers have same formula but different connectivity.
(iii) Enantiomers are non-superimposable mirror images.
(iv) Diastereomers are conformers.

e) Which of the following compounds exhibit planar chirality

i) 

ii) 

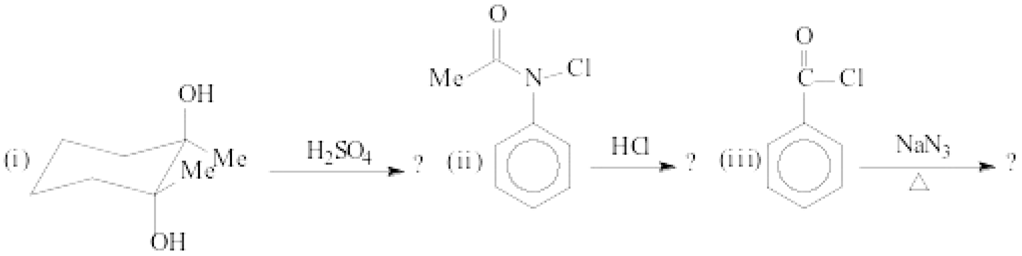
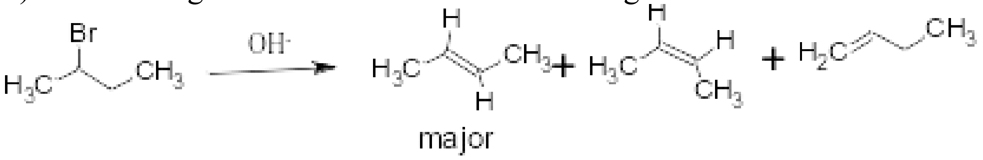
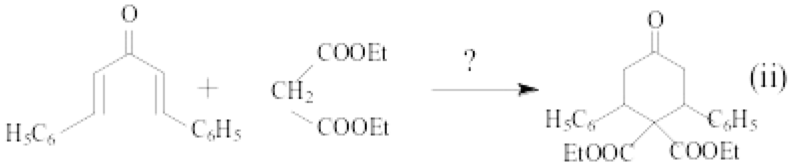
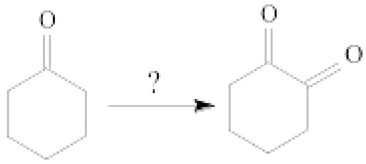
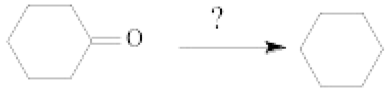
iii) 

iv, 

SECTION A – K2 (CO1)

Answer ALL the questions **(5 x 1 = 5)**

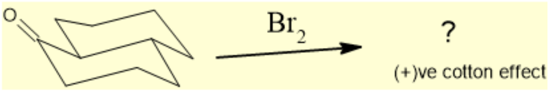
2 True or False

a)	The trapping agent for the intermediate nitrene is benzene.
b)	The driving force of the Claisen rearrangement is thermodynamically C-alkylation is more stable than O-alkylation.
c)	Hydroboration of alkene follows Markovnikov addition.
d)	Dissymmetry compounds possess chiral centers.
e)	Cis-decalin is obtained by the fusion of axial and equatorial bonds.
	SECTION B – K3 (CO2)
	Answer any THREE of the following **(3 x 10 = 30)**
3	Discuss the importance of the following methods in determining the reaction mechanism. (4+3+3) (i) Direct isolation of the intermediates (ii) Product analysis (iii) Trapping of an intermediate.
4	Predict the product and outline the mechanism for the following reactions: (3+4+3) 
5	Highlight any one synthetic use of the following reagents giving mechanism. (4+3+3) (i) DMSO-DCC (ii) HIO_4 (iii) $LiAlH_4$
6	Describe the different methods used for (i) racemization and (ii) resolution of racemic modification. (5+5)
7	a) Show the significance of conformation in the given stereoselective reaction. (6)  b) trans-2-Iodocyclohexyl brosylate undergoes acetolysis rapidly compare to the cis-isomer. Justify. (4)
	SECTION C – K4 (CO3)
	Answer any TWO of the following **(2 x 12.5 = 25)**
8	(a) The reaction of benzoin condensation and base-catalyzed iodination of acetone follows 3rd order kinetics. Justify with mechanism. (6.5) (b) Explain the mechanism of the following rearrangements: (3+3) (i) Favorskii (ii) Wolff
9	Convert the following choosing suitable reagent/s with mechanism. (4.5+4+4) (i)  (ii)  (iii) 
1	(a) Examine the nature of chirality and rules for assigning configuration for spiranes and *trans*-cyclooctene compounds. (8)

0 (b) Explain prochirality with examples. (4.5)

11 (a) Investigate the steps involved in Sharpless asymmetric epoxidation reaction. (8)

(b) The product obtained in the given conversion shown positive cotton effect. Deduce the configuration of the resultant product. (4.5)

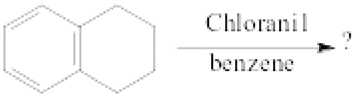


SECTION D – K5 (CO4)

Answer any ONE of the following **(1 x 15 = 15)**

12 (a) Derive the Hammett equation and highlight its salient features. (6)
(b) Explain the mechanism of a pinacol-pinacolone rearrangement involving a ring-contraction and ring-expansion reactions. (5)
(c) Predict the product/s. (4)

(i)



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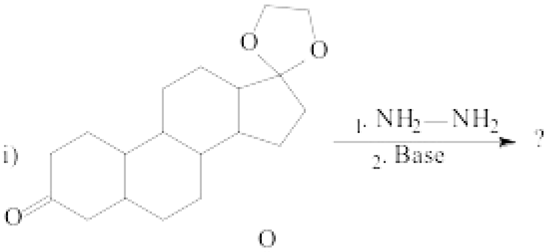

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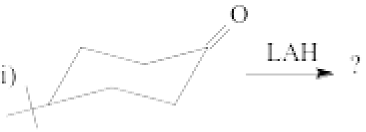

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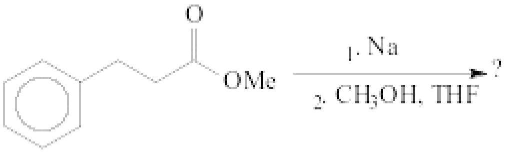
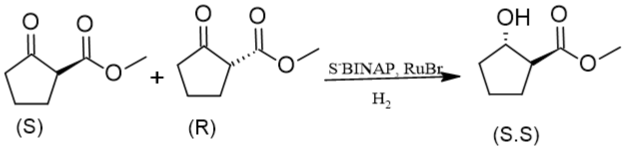


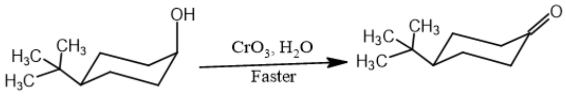
13 (a) Exemplify the application of chiral solvating agents in determining enantiomeric proportion. (4)

(b). Justify the following asymmetric induction reaction using Curtin-Hammett principle. (6)



(c). Account for the difference in the rate of the following reactions. (5)

i.



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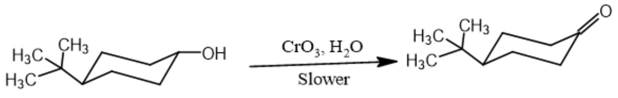


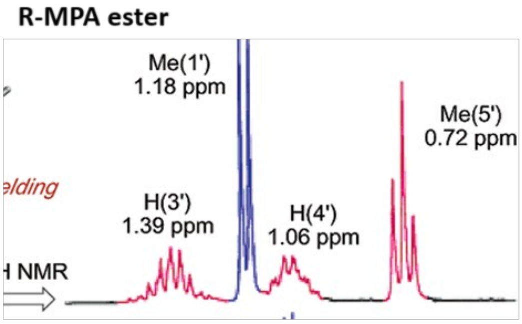
SECTION E – K6 (CO5)

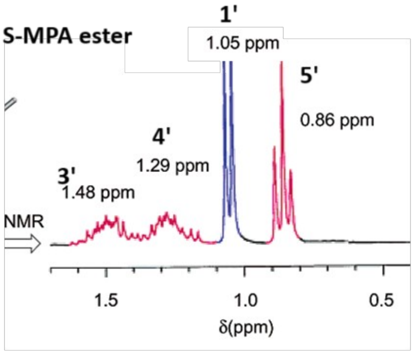
Answer any ONE of the following **(1 x 20 = 20)**

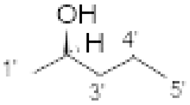
14 (a) Explain the types of kinetic isotope effect with example. (5)
(b) “Bromination of isobutane is more selective than chlorination”. Justify. (5)
(c) Write the mechanism of the following rearrangements: (5)
(i) *Inter*-molecular Fries (ii) Dienone-phenol

(d) Outline the effect of -R and +R substituents on a Birch reduction with mechanism. (5)

15 a) Deduce the configuration of 2-pentanol using the given NMR spectra of the R/S MPA ester. (6)



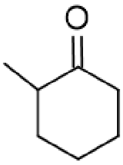




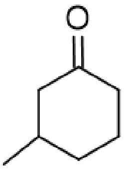
b) Propose suitable catalysts and conditions to achieve efficient enantioselective reduction of ketones. (4)

c) Compile the type of cotton effects exhibited by the given methyl cyclohexanones both at axial and equatorial positions. (6)

i.



ii



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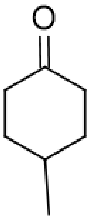
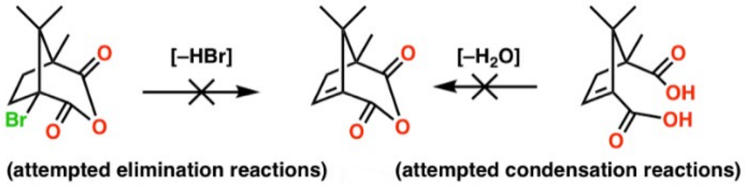
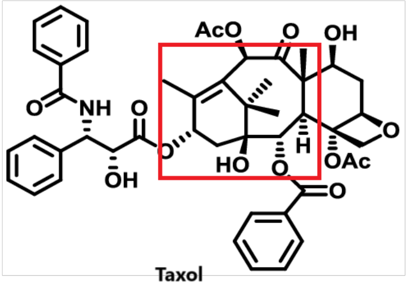


d) Account for the failure of the following transformations using a suitable rule. How do you then account for the existence of similar systems in natural products such as Taxol? (4)





Taxol
