LOYOLA COLLEGE (AUTONOMOUS) CHENNAI – 600 034

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

FIRST SEMESTER – **APRIL 2025**

PCH1MC01 – ORGANIC REACTION MECHANISM AND STEREOCHEMISTRY

Date: 23-04-2025 Dept. No. Max. : 100 Marks

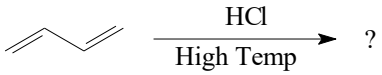
Time: 09:00 AM - 12:00 PM

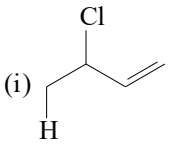
SECTION A – K1 (CO1)

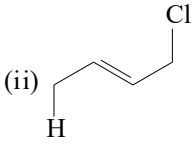
Answer ALL the questions **(5 x 1 = 5)**

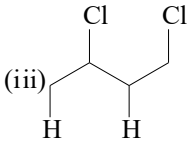
1 MCQ

a) The major product of the following reaction is



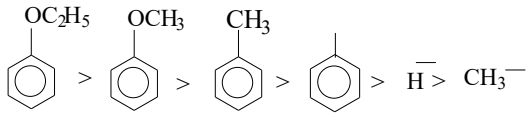
(i) 

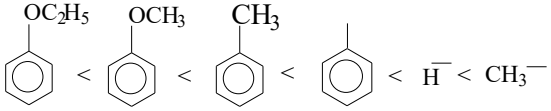
(ii) 

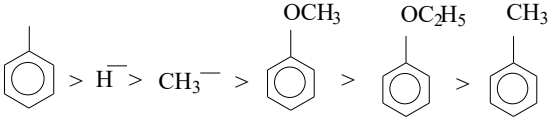
(iii) 

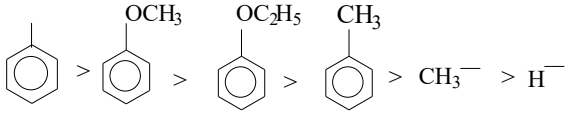
(iv) All of these

b) The order of migratory aptitude for pinacol-pinacolone rearrangement is

(i) 

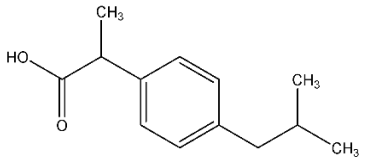
(ii) 

(iii) 

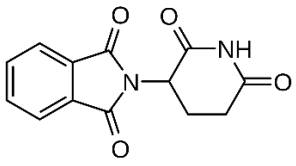
(iv) 

c) Which of the following reaction does not have any kinetic isotope effect?
(i) Solvolysis of t-butyl chloride in 60% aqueous ethanol.
(ii) Elimination of HBr from 2-bromopropane in C_2H_5ONa.
(iii) Bromination of acetophenone in base.
(iv) Nitration of benzene.

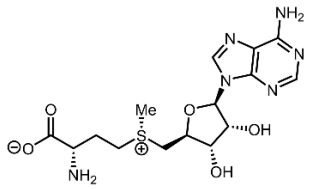
d) Identify the dissymmetric compound among the given compounds.

i. 

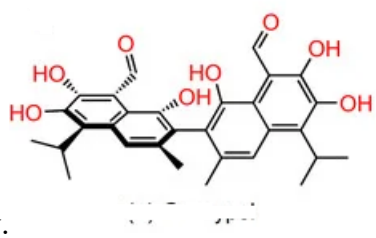
Ibuprofen

ii. 

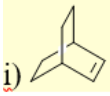
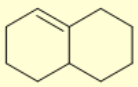
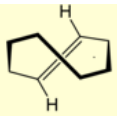
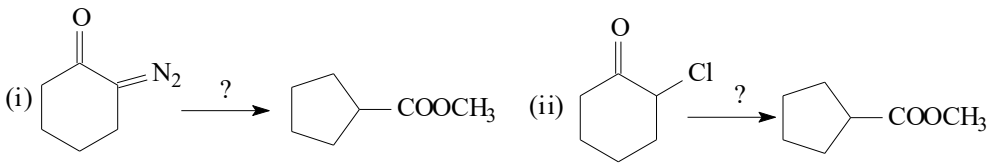
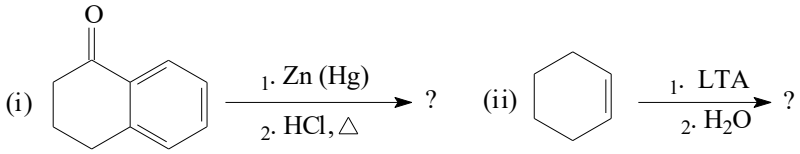
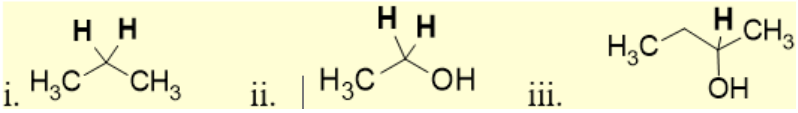
pthalidoamide

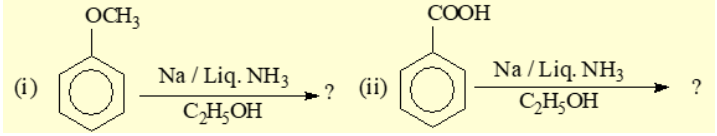
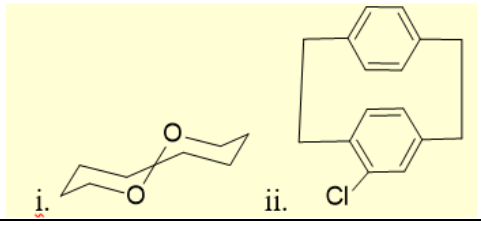
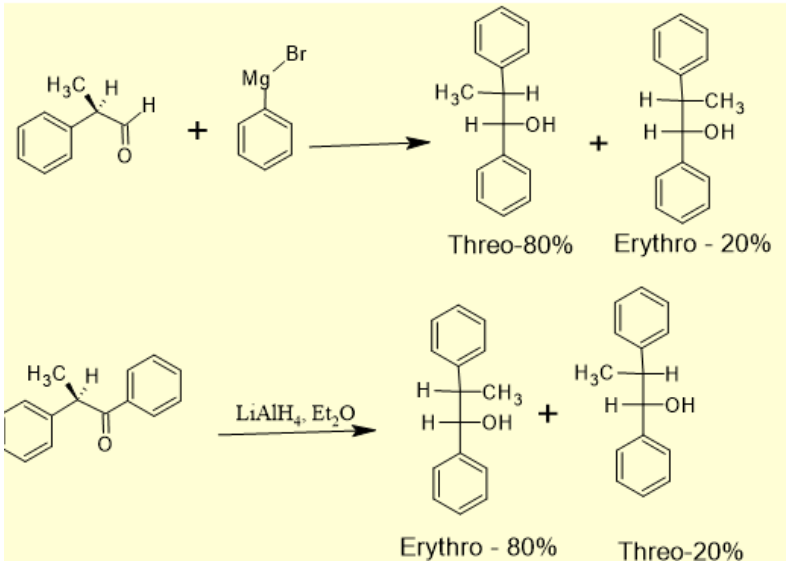
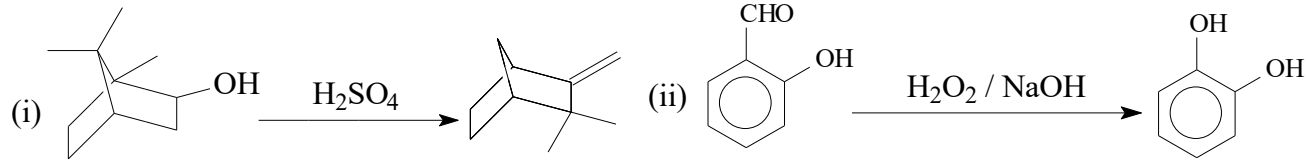
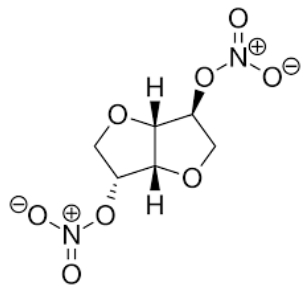
iii. 

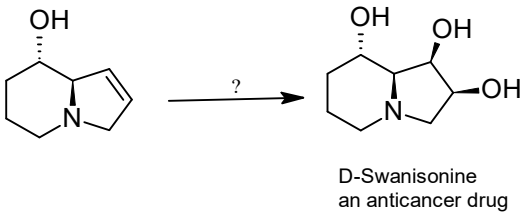
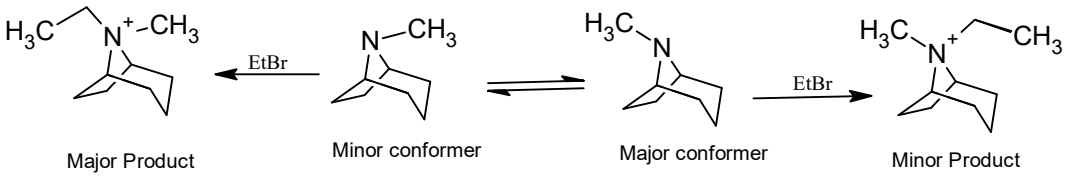
SAM

iv. 

Gossypol

e)	Which of the following is not a stable compound? i)  ii.  iii.  iv. 
	SECTION A – K2 (CO1)
	Answer ALL the questions **(5 x 1 = 5)**
2	**True or False**
a)	Bromination of an alkane is more selective and exothermic reaction.
b)	The conversion of α-diazo ketone into an ester is called Dakin rearrangement.
c)	Benzoin condensation is a 2nd order reaction.
d)	Enantiomers have different physical properties.
e)	Conformers are isomers having the same bond connectivity sequence and can be interconverted by rotation around one or more single bonds.
	SECTION B – K3 (CO2)
	Answer any THREE of the following **(3 x 10 = 30)**
3	Explain the importance of Hammond postulate in determining the structure of intermediates in halogenation of isobutane with mechanism and reaction coordinate diagram.
4	Predict the mechanism of the following conversions choosing suitable reagent/s and give the name of reactions. (5+5) 
5	(a) Compare the hydride reduction of $LiAlH_4$ and $NaBH_4$ with suitable examples. (5) (b) Predict the product of the following reactions through mechanism. (2 x 2.5) 
6	Analyse the nature of topicity of the highlighted hydrogens in the given compounds. (4+4+2) 
7	Construct and explain the energy profile diagram of n-butane conformers.
	SECTION C – K4 (CO3)
	Answer any TWO of the following **(2 x 12.5 = 25)**
8	(a) Prove that the sulphonation of benzene reaction follows microscopic reversibility. (4) (b) How would you determine the mechanism of acid-catalyzed hydrolysis of an ester? (4) (c) The dehydrobromination of 2-phenyl ethyl bromide in C_2H_5ONa/C_2H_5OH has the k_H/k_D = 7.1. Propose the mechanism for this reaction. (4.5)

9	(a) Explain the salient features of the following rearrangements: (i) Abnormal Beckmann (ii) Abnormal Claisen	(3+3.5)
	(b) Explain any one synthetic use of aqueous $KMnO_4$ and OsO_4 with mechanism.	(3+3)
10	(a) Predict the product and compare the mechanism of the following reactions. 	(6.5)
	(b) Predict the nature of chirality and assign the configuration of the given compounds. 	(3+3)
11	(a) Examine the following stereoselective reactions based on appropriate rules. 	(4+4)
	(b) Compare the stabilities of the conformers of 1,2 and 1,3 dimethyl cyclohexanes.	(4.5)
	SECTION D – K5 (CO4)	
	Answer any ONE of the following	**(1 x 15 = 15)**
12	(a) Explain the significance of the Von-Richter reaction in determining the mechanism of the reaction.	(5)
	(b) Outline the mechanism of the following conversions. 	(5+5)
13	(a) Using Cahn-Ingold-Prelog rules, determine the configuration at each chiral centre present in isosorbide dinitrate, a drug used to prevent chest pain. 	(5)

	(b) Explain the different methods used for the resolution of racemic modification. (4) (c) Propose a suitable method for the following asymmetric transformation and evaluate the mechanism involved. (6)  D-Swanisonine an anticancer drug
	SECTION E – K6 (CO5)
	Answer any ONE of the following **(1 x 20 = 20)**
14	(a) Mechanistic implications of rate law of a diazotization of aniline. (5) (b) Explain the mechanism of the following rearrangements: (5+5) (i) Baeyer-Villiger (ii) Hofmann-Martius (c) Outline the mechanism of McFadyen-Stevens reduction. (5)
15	(a) Discuss the application of chiral derivatizing and solvating agents in determining the absolute configuration and enantiomeric composition of chiral compounds using NMR technique. (6) (b) Rationalise the product proportion in the given conversion using Curtin-Hammet principle. (7)  Major Product Minor conformer Major conformer Minor Product (c) R(+)-3-Methylcyclohexanone exhibits positive cotton effect. Determine the stable conformation at the chiral centre. (7)
