LOYOLA COLLEGE (AUTONOMOUS), CHENNAI – 600 034

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

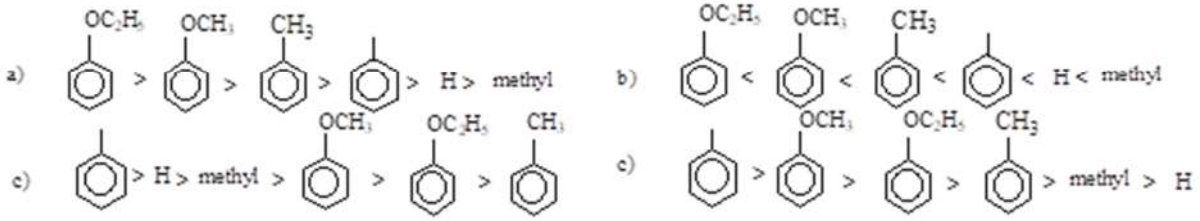
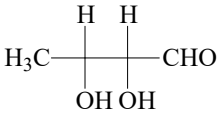
FIRST SEMESTER – **NOVEMBER 2023**

PCH1MC01 – ORGANIC REACTION MECHANISM AND STEREOCHEMISTRY

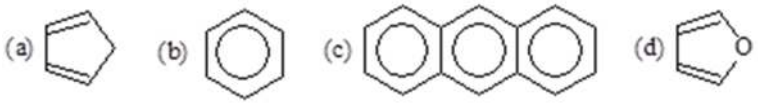
Date: 31-10-2023 Dept. No. Max. : 100 Marks

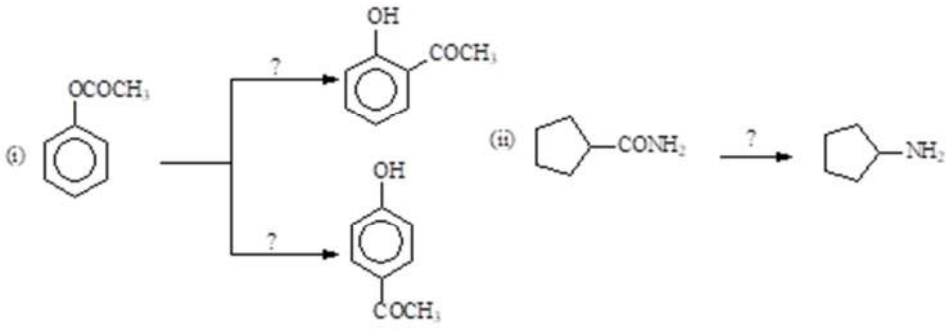
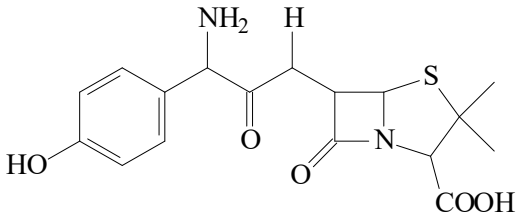
Time: 01:00 PM - 04:00 PM

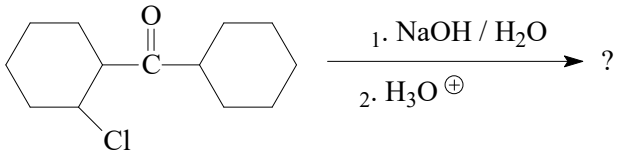
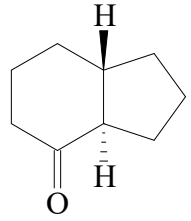
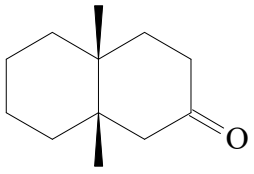
SECTION A – K1 (CO1)

	Answer ALL the questions	**(5 x 1 = 5)**
1	**Choose the correct answer.**	
a)	The species that can be classified as electron sources are i) R in RMgX ii) Lewis acids iii) Carbon in C-Cl (alkyl halide) iv) Carbon in C-Li (alkyl lithium) v) H in $LiAlH_4$ (a) Only (i), (iv) and (v) (b) All of these (c) None of these (d) (i) and (iv) only	
b)	The order of migratory aptitude in pinacol-pinalcolone rearrangement is  	
c)	The intense blue solution formed in Birch reduction is due to the a) formation of NH_2 and H_2 b) formation of $NH_3 + e^-$ c) formation of $Li^+ + e^- [NH_3]_n$ d) ethanol	
d)	The correct name of the given compound is_____.  a) 2(*R*), 3(*R*)-2,3-dihydroxybutanal b) 2(*S*), 3(*R*)-2,3-dihydroxybutanal c) 2(*R*), 3(*S*)-2,3-dihydroxybutanal d) 2(*S*), 3(*S*)-2,3-dihydroxybutanal	
e)	The product formed between the reaction of *trans*-2-aminocyclohexanol with HNO_2 is a) cyclopentyl aldehyde b) cyclohexanone c) both a & b d) cyclohexane	

SECTION A – K2 (CO1)

	Answer ALL the questions	**(5 x 1 = 5)**
2	**Choose the correct answer.**	
a)	Benzyne can be trapped by _____.  	
b)	The reagents used for the conversion of benzil into benzilic acid is a) Me_3COK / Me_3COH b) $KOH/C_2H_5OH/H_2O$ c)$NaOH/H_2O$ d) All the above	
c)	Which of the following order is correct with LAH as reducing agent? a) ester > amide > carboxylic acid > ketone > aldehyde	

	b) carboxylic acid > amide > ester > ketone > aldehyde c) aldehyde > ketone > ester > amide > carboxylic acid d) aldehyde < ketone < ester < amide < carboxylic acid
d)	Which of the following compounds contains diastereotropic protons? a) ethyl chloride b) 1,2-dichloropropane c) 2-methylpropene d) 1,2-dicholroethane
e)	The stereoeletronic requirement for a molecular elimination reaction is_____. (a) *anti* (b) *cis* (c) both a & b (d) none of these
	SECTION B – K3 (CO2)
	Answer any THREE of the following **(3 x 10 = 30)**
3	a) Construct the potential energy diagram for the reaction between 1,3-butadiene and HBr and compare the percentage yield of the products. (5) b) Predict the mechanism of an acid-catalysed and base-catalysed hydrolysis of ethyl acetate using an isotopically labelled atom? (5)
4	Make use of suitable reagent/s and conditions and explain the mechanism of the following conversions. (5+5) 
5	Identify any one synthetic application for the following reagents and explain with mechanism. (4x 2.5) (i) SeO_2 (ii) HIO_4 (iii) LTA (iv) MnO_2
6	a) Explain the use of chiral derivatizing agents (CDA) in NMR spectral characterization of enantiomers. (5) b) Identify the number of chiral centers present in the given amoxicillin drug molecule and designate R / S notation. (5) 
7	Discuss the following. a) Base induced dehydrohalogenation reaction of erythro-1-bromo-1,2-diphenylpropane undergoes much slower rate than its *threo* isomer. (5) b) Prove that the rate of racemisation is twice the rate of interconversion in a racemic modification process. (5)
	SECTION C – K4 (CO3)
	Answer any TWO of the following **(2 x 12.5 = 25)**
8	(a) Analyse the formation of carbene and benzyne intermediates and suggest any one method of Detection. (6.5) (b) Compare the mechanism of the following rearrangements: (i) Lossen (ii) Schmidt (3+3)

9	a) Predict the product with mechanism for the following. (6.5)  b) Discuss the mechanism of the following reduction reactions. (3+3) (i) McFadyen-Stevens (ii) Bouveault-Blanc
10	(a) Explain the chemical method of racemisation by anion intermediate formation with suitable example. (6) (b) Explain the racemic modification of enantiomers by reversible formation of stable inactive intermediates with two examples. (6.5)
11	(a) Apply Curtin Hammett principle on the dehydrohalogenation of 2-bromobutane and explain the role of transition state in the product prediction.(6) (b) Discuss the pyrolysis reaction of cis and trans-2-phenylcyclohexylxanthates. (6.5)
	SECTION D – K5 (CO4)
	Answer any ONE of the following **(1 x 15 = 15)**
12	Explain the following. (5 + 5 + 5) (i) Mechanistic implications of rate law for benzoin condensation. (ii) Ring contraction and ring expansion in Pinacol-Pinacolone rearrangement. (iii) Effect of substituents on Birch reduction.
13	(a) Explain chelate and dipolar models of Cram's rule in the asymmetric induction reactions. (8) (b) Explain regioselective and stereoselective syntheses with suitable examples. (7)
	SECTION E – K6 (CO5)
	Answer any ONE of the following **(1 x 20 = 20)**
14	(a) Discuss the special features of von-Ritcher reaction with mechanism. (5) (b) Derive Hammett equation and explain the effect of substituents on rate and substituent constants value. (5) (c) Describe the mechanistic pathway of (5 + 5) (i) Hydroboration reaction (ii) Oxidation of alcohol by DMSO-DCCD
15	(a) Analyse the stereochemistry of the acetolysis reaction of 2-phenyl-3-pentyl tosylate and 3-phenyl-2-pentyl tosylate. (8) (b) Explain the following with suitable examples: (3 + 3) (i) second order asymmetric transformation (ii) resolving agents (c) Apply octant rule and predict the cotton effect for the following cyclic ketones. (6) (i)  (ii) 

&&&&&&&&&&