	LOYOLA COLLEGE (AUTONOMOUS), CHENNAI – 600 034						
M.Sc. DEGREE EXAMINATION – CHEMISTRY							
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-00	PCHIMCOI – ORGANIC REACTION MECHANISM AND STEREOCHE	W151	RY				
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11	me. 01.00 f m - 04.00 f m						
	SECTION A						
An:	/er ALL the Questions $(5 \times 1 - 5)$						
			1 = 3)				
a)	(a) Reformatsky reaction (b) Aldol condensation	K 1	CO1				
	(c) von-Ritcher reaction (d) Reimer-Tiemann reaction.		COI				
b)	The product of the following reaction is						
		IZ 1	CO1				
		KI	COI				
	CH ₂ CH ₂						
	a) CH_2 b) c) d)						
	CH ₂						
c)	Which of the following statement is incorrect?						
	a) LTA is used for the cleavage of 1,2-glycols b) HIQ, is used for the cleavage of 1,2 glycols to carbonyl	K1	COL				
	c) LTA and HIO ₄ are less selective reagents	NI I	COI				
	d) <i>cis</i> -glycols cleaved more easily than <i>trans</i>						
d)	Which of the following is resolvable into enantiomers?						
	a) trans-1,3-cyclohexane diol b) <i>trans</i> -1,4-cyclohexane diol	K1	CO1				
	c) <i>cis</i> -1,2-cyclohexane diol d) <i>cis</i> -1,4-cyclohexane diol						
e)	The reaction of erythro 1-bromo-1.2-diphenylpropane with alcoholic KOH gives						
	a) (Z)-1 2-diphenyl-1propene b) (E)-1 2-diphenyl-1propene	K1	CO1				
	c) both (Z) and (E)-1.2-diphenyl-1propene d) 1.2-diphenyl-1propanol		001				
2	Choose the correct answer	(5 x 1	= 5)				
a)	Which of the following statement is correct with Hammett equation?	Ì	, 				
<i>a)</i>	(a) When $\rho > 1$, reaction is more sensitive than benzoic acid and intermediate is						
	negatively charged.						
	(b) When $\rho < 1$, reaction is more sensitive than benzoic acid and intermediate is	K2	CO1				
	Negatively charged.		001				
	(c) when p<1, reaction is more sensitive than benzoic acid and intermediate is positively charged						
	(d) If $\rho = 0$, reaction has more substituent effect.						
b)	The correct order of migratory aptitude for Baeyer-Villiger rearrangement is						
	a) tertiary alkyl > sec.alkyl , aryl, benzyl > primary alkyl > methyl						
	b) sec.alkyl, aryl, benzyl >tertiary alkyl > primary alkyl > methyl	K2	CO1				
	d) methyl > tertiary alkyl > sec alkyl aryl benzyl > methyl						
	a, meany / vertuary arky / sociarky (ary), oonzy / primary arky	1	<u> </u>				

c)	The product of the following reaction is		
	\sim \downarrow \downarrow LTA		
	OOHO	K2	CO1
	O O O		
d)	Bacemic modification can be achieved by		
	a) First order asymmetric transformation b) the use of enzymes	К2	CO1
	c) Second order asymmetric transformation d) all the above		001
e)			
0)	Which among the following will exhibit +ve Cotton		
	a) b) H c) o H effect?	K2	CO1
	CH ₃ CH ₃ Ö		
	SECTION B		
	Answer any THREE of the following (3	x 10 :	= 30)
3	Show the mechanism and potential energy diagram for kinetically controlled and		
	thermodynamically controlled product formation of a reaction between 1,3-butadiene	K3	CO2
	and HBr.		
4	Construct the mechanism for the following rearrangements choosing a suitable	V 2	CO2
	example for each: (i) Hoffmann rearrangement (ii) Benzil-benzilic acid	КЭ	02
5	Sketch the mechanism for the following reactions:		
			~~~
	(i) $(i) O_3 \rightarrow ?$ (ii) $(i) O_3 \rightarrow ?$	K3	CO2
	(ii) $H^+/H_2O$		
6	a) Explain the chemical method of racemisation through anion intermediate formation		
Ŭ	(5)	K3	CO2
	b) Discuss the optical isomerism exhibited by biphenyls and spiranes. (5)	_	
7	(a) Discuss the stereochemistry of the acetolysis reaction of 2-phenyl-3-pentyl tosylate		
	and 3-phenyl-2-pentyl tosylate. (8)	K3	$CO^{2}$
	(b) How the stable conformation of 1,2-dibromocyclohexane is classified by dipole	KJ	002
	moment measurements? (2)		
	SECTION C		
	Answer any TWO of the following (2 x	x 12.5	= 25)
8	(a) "Bromination of 2-methyl propane is more selective than chlorination". Explain		
	(6) with mechanism and potential energy diagram.	K4	CO3
	(b) Derive Hammett equation and explain the effect of substituents upon the acidity		_
0	(0.5) (0.5) (0.5)		
9	(a) Explain the mechanism of beckmann rearrangement. (b) Predict the product and explain the mechanism of the following reactions: (6.5)		
	/ (0.5)		
	← CHO -	K4	CO3
	(i) $CF_3CO_3H$ (ii) $H_2O_2/OH$ ?		
10	(a) Explain the mechanism of any one synthetic applications $aq.CrO_3$ and acidified		
	(6) (6) (6)	K4	CO3
	(D) Explain the use of chiral derivatizing agents (CDAs) in NMR spectral techniques		
11	(a) Why the deamination of (Ph)(Ph')(OH)CCH(NH ₂ )CH ₂ does not follow		
11	Curtin-Hammet principle? Explain (7)	K4	CO3
	(/)		

	(b) Explain the pyrolysis reaction of xanthates.	(5.5)					
SECTION D							
Answer any ONE of the following (1				= 15)			
12	<ul> <li>(a) Summarize the role of the following methods in determining the reaction mechanism: (i) Product analysis (iii) Detection of reaction intermediates</li> <li>(b) Predict the mechanism of the following reaction:</li> <li>Cl</li> <li>Cl</li> <li>NaOCH₃</li> <li>COOCH₃</li> <li>(c) Predict the product of the following reaction with mechanism:</li> <li>COOH</li> <li>(i) Na /liq. NH₃</li> <li>(ii) DDQ</li> <li>(ii) DDQ</li> </ul>	(6) (4)	K5	CO4			
	$(1) \qquad \qquad EtOH \qquad ? \qquad (1) \qquad \qquad$						
13	<ul> <li>Discuss about the following.</li> <li>(a) Reaction of <i>cis &amp; trans</i> 2-aminocyclohexanol with HONO.</li> <li>(b) Reaction of erythro-3-bromo-2-butanol with HBr.</li> <li>(c) 2-alkylketone effect</li> </ul>	(5) (5) (5)	K5	CO4			
	SECTION E			<u> </u>			
Ans	swer any ONE of the following	(1	x 20 =	= 20)			
14	<ul> <li>(a) Write brief explanatory notes on the following methods in determination of the reaction mechanism:</li> <li>(i) Addition of a suspected intermediate in von-Ritcher rearrangement.</li> <li>(ii) Mechanistic implications of rate law of diazotization of aniline and benzoin condensation reaction.</li> <li>(b) Compile the mechanism of <i>para</i>- Claisen and abnormal Claisen rearrangement</li> <li>(c) Predict the product and write the mechanism of the following reactions.</li> </ul>	(8) n (6)	K6	CO5			
15	$COOC_2H_5$						
15	(a) write the mechanism of McFadyen-Steven's and MPV reduction. (b) Classify the following as point/axial/plane chiral molecules and assign R/S notation. (c) $H_{HH}$ (c) $H_{HH}$ (c) $H_{HH}$ (c) $H_{Ha}$ (c)	(0) (8)	K6	CO5			
	(c) Explain Cram's and Prelog rules with suitable examples.	) +3)	<u> </u>	[]			
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