LOYOLA COLLEGE (AUTONOMOUS) CHENNAI – 600 034

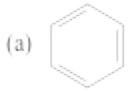
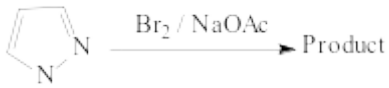
M.Sc. DEGREE EXAMINATION – **CHEMISTRY**

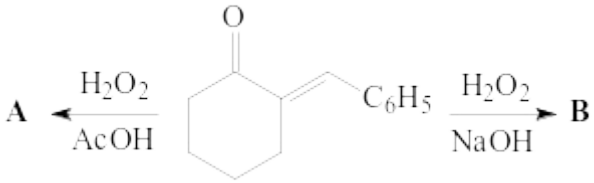
SECOND SEMESTER – **NOVEMBER 2024**

PCH2MC01 – ORGANIC REACTION MECH. AND HETEROCYCLIC COMPOUNDS

Date: 11-11-2024 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.	**Multiple choice questions**
a)	Which of the following compounds is anti-aromatic? (a)  (b)  (c)  (d) 
b)	The number of ESR lines given by a methyl radical are (a) 4 (b) 5 (c) 6 (d) 7
c)	Which of the following is not involved in Rosenmund reduction? (a) Acid chloride (b) H_2 (c) Pd-$BaSO_4$ (d) Aluminium isopropoxide
d)	The compound/s which does not undergo Markovnikov's addition is/are_____. (i) CH_2=C=CH_2, (ii) CH_2=C=O, (iii) CH_2=CH-CF_3 (a) (iii) only (b) (ii) & (iii) (c) (ii) only (d) all of these
e)	Predict the substitution position for bromination in the following reaction.  (a) 3rd position (b) 4th position (c) 5th position (d) 2nd position
	SECTION A – K2 (CO1)
	Answer ALL the questions **(5 x 1 = 5)**
2.	**Multiple choice questions**
a)	Which of the following statement is incorrect? (a) Anti-aromatic compounds are more stable than non-aromatic compounds. (b) Cyclooctatetraene is a tub-shaped molecule. (c) Homoaromatic compounds contain a sp^3 hybridized carbon. (d) Aromatic compounds obey Huckel's 4n+2 rule.
b)	The intermediate in S_N1 reaction is a (a) radical (b) carbanion (c) carbocation (d) carbene
c)	Which of the following statement/s is/are correct? (a) E1 reaction follows Saytzeff rule. (b) E2 reaction never gives Hofmann product. (c) E1cb reaction occur under acidic conditions. (d) All of these
d)	Benzyne + anthracene forms (a) triptycene (b) naphthalene (c) phenanthrene (d) all of these
e)	Imidazole on reaction with nitrating mixture forms

	(a) 4-nitroimidazole (b) 2-nitroimidazole (c) 5-nitroimidazole (d) none
	SECTION B – K3 (CO2)
	Answer any THREE of the following **(3 x 10 = 30)**
3.	(a) Compare the conditions for aromatic, non-aromatic and anti-aromatic nature of compounds. (5) (b) Explain the mechanism and limitations of Friedel Crafts acylation. (5)
4.	(a) Which of the following will undergo solvolysis more readily and why? (5) $(C_6H_5)_2CHBr$ or $(CH_3)_3CBr$ (b) Explain S_NAr reaction mechanism with suitable evidences. (5)
5.	Discuss the mechanism and evidences of E1 reaction.
6.	(a) Predict the product for the reaction of cyclohexenone with Gilman reagent. (4) (b)Why are alkynes less reactive towards addition reaction than alkenes? (3) (c) "Wittig reagents are carbon nucleophiles." Justify this statement. (3)
7.	How are 1,3-oxazole and thiazoles synthesised by Hantzsch method? Discuss the substitution position with anelectrophilie? (10)
	SECTION C – K4 (CO3)
	Answer any TWO of the following **(2 x 12.5 = 25)**
8.	(a) Discuss the orientation and reactivity of nitrobenzene. (6) (b) Write the mechanism and uses of Stark-enamine reaction. (6.5)
9.	(a) Explain the Gomberg method of the formation of triphenyl methyl radical. (6.5) (b) How would you detect a long-lived and a short-lived free-radicals? Explain. (6)
10.	(a) Account for the following statements: (i) Stereospecificity of bromination reaction of $PhCH=CHCH_3$ decreases in solvents of high dielectric constant. (4) (ii) Addition of Br_2 in ethylene in methanol solvent is retarded by the addition of KBr and results in the formation of a mixture of $Br\text{-}CH_2\text{-}CH_2\text{-}Br$ and $Br\text{-}CH_2\text{-}CH_2\text{-}OCH_3$. (4) (b) How is 1,3-oxazole synthesised by Robinson-Gabriel synthesis? (4.5)
11.	(a) Identify A & B and justify your answer with suitable mechanism. (4+4)  (b) What is Grunwald-Winstein relationship? (4.5)
	SECTION D – K5 (CO4)
	Answer any ONE of the following **(1 x 15 = 15)**
12.	(a) Explain the aromaticity of [10]-, [14]-, and [18]-annulenes. (9) (b) Explain single electron transfer mechanism (SET) with evidences. (6)
13.	(a) 'The effect of attacking nucleophile in S_N1 reaction kinetics is negligible.' Why? (5) (b) Explain Sommelet-Hauser rearrangement with mechanism. (5) (c) Draw the resonance structures of 1,2,3-triazole and tetrazole and explain their reactivity towards electrophilic substitution reactions. (5)
	SECTION E – K6 (CO5)
	Answer any ONE of the following **(1 x 20 = 20)**
14.	(a) Illustrate the mechanism, evidences, orientation and reactivity of E2 reaction. (12) (b) Give the evidences for the syn, anti, and non-stereoselective electrophilic addition of olefins. (8)
15.	(a) Predict the product for the addition of carbenes to *trans*-2-butene in gaseous and liquid phases. (5)

	(b) Identify the position of an electrophilic substitution in the 1,2-azoles and write the nitration, halogenation reactions on pyrazoles and isothiazoles. (10) (c) Write any one method of synthesis for pyridazine. (5)
