LOYOLA COLLEGE (AUTONOMOUS), CHENNAI – 600 034

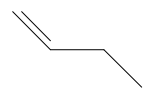
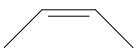
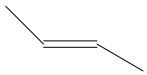
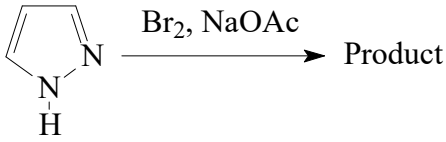
M.Sc. DEGREE EXAMINATION – **CHEMISTRY**

SECOND SEMESTER – **APRIL 2024**

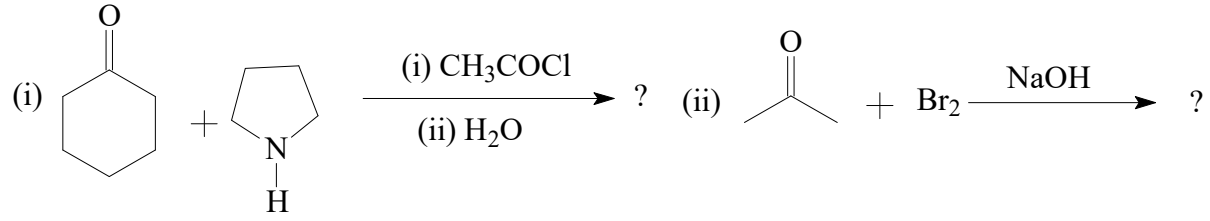
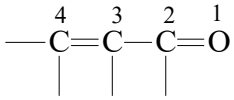
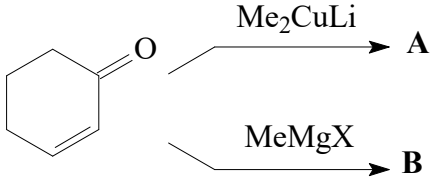
PCH2MC01 – ORGANIC REACTION MECH. AND HETEROCYCLIC COMPOUNDS

Date: 04-04-2024 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 compound is non-aromatic? (i) Benzyne (ii) Cyclobutadiene (iii) Cyclooctatetraene (iv) All of these	
b)	The intermediate in an α-elimination reaction is (i) Carbene (ii) Carbocation (iii) Carbanion (iv) Carbon free-radical	
c)	The isolable intermediate formed in the Bucherrer reaction of naphthol into naphthyl amine is _____. (i) tetralone (ii) sulphonic acid of tetralone (iii) naphthaquinone (iv) naphthyl sulphonic acid	
d)	Which among the following on reaction with H_2SO_4 & H_2O will form 2-butanol? (i)  (ii)  (iii)  (iv) all the above	
e)	Predict the substitution position of the bromination reaction in the following.  (i) 3rd position (ii) 4th position (iii) 5th position (iv) 2nd position	
	SECTION A – K2 (CO1)	
	Answer ALL the questions	**(5 x 1 = 5)**
2	**State whether the following statements are True or False**	
a)	All fulvenes are non-aromatic.	
b)	The orientation of E1 is always Saytzeff.	
c)	In an aromatic nucleophilic substitution reaction electron withdrawing substituent on benzene activates reaction.	
d)	Maleic acid on reaction with Br_2 forms *dl*-2,3-dibromosuccinic acid.	
e)	Acetyl acetone on reaction with hydrazine in presence of aq. NaOH forms pyrazole.	

SECTION B – K3 (CO2)

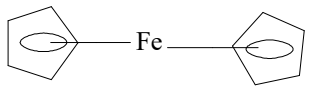
	Answer any THREE of the following	**(3 x 10 = 30)**
3	(a) Explain the arenium-ion mechanism. (4) (b) Predict the product/s and give mechanism. (3+3) 	
4	Explain the mechanism, stereochemistry of E1 reaction with evidences.	
5	Explain the following with examples. (a) Benzyne mechanism (b) Sommelet-Hauser rearrangement (5 + 5)	
6	(a) Explain single electron transfer mechanism with suitable example and evidences. (6) (b) Why does nucleophilic addition never occur at C-3? (4) 	
7	(a) Identify the products A & B and justify your answer. (3 + 3)  (b) How are 1,3-oxazole and thiazoles obtained by Robinson-Gabriel synthesis? (4)	

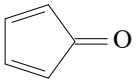
SECTION C – K4 (CO3)

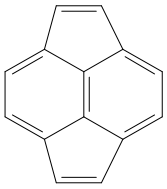
	Answer any TWO of the following	**(2 x 12.5 = 25)**
8	(a) The bromination of toluene using bromine in aqueous acetic acid takes place 605 times faster than the bromination of benzene. The product ratio is 32.9% *ortho*-, 0.3% *meta*-, and 66.8% *para*-bromotoluene. Calculate the partial rate factors for the reaction with mechanism. (6.5) (b) Illustrate the mechanism, stereochemistry and evidences of S_E^2 reaction with an example. (6)	
9	(a) Explain the Gomberg method of formation and detection of free-radicals. (6) (b) CH_3-Br reacts with AgCN to give CH_3NC, whereas it reacts with NaCN to give CH_3CN. Justify.(4) (c) What is Grunwald-Winstein relationship? (2.5)	
10	(a) Explain ion-pair mechanism with suitable example and evidences. (8) (b) "Stereospecificity of bromination of $PhCH=CHCH_3$ decreases in solvents of high dielectric constant" Explain. (4.5)	
11	(a) Give the evidences for the *syn*-, *anti*-, and *non*-stereoselective electrophilic addition of olefins. (8) (b) Discuss the electrophilic substitution reactions in 1,3-azoles with suitable examples. (4.5)	

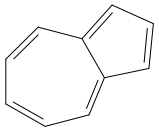
SECTION D – K5 (CO4)

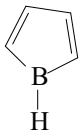
	Answer any ONE of the following	**(1 x 15 = 15)**
12	(a) Predict the aromaticity of the following compounds applying conditions.	(5)

(i) 

(ii) 

(iii) 

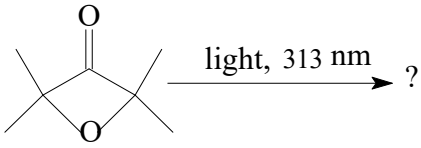
(iv) 

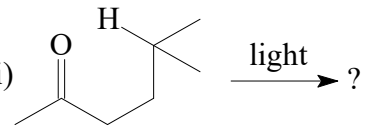
(v) 

	(b) Illustrate the orientation and reactivity of E2 reaction using suitable example.	(5)
	(c) Explain any one method of formation and detection of short-lived free radicals.	(5)
13	(a) Explain the influence of solvent towards the aliphatic nucleophilic substitution reaction.	(5)
	(b) Prove that nucleophilic substitution at vinylic carbon occurs through addition-elimination mechanism.	(5)
	(c) Explain Simon-Smith reaction with suitable examples.	(5)

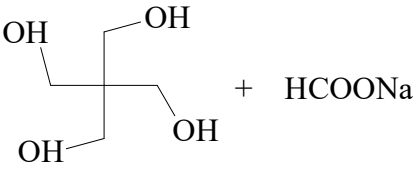
SECTION E – K6 (CO5)

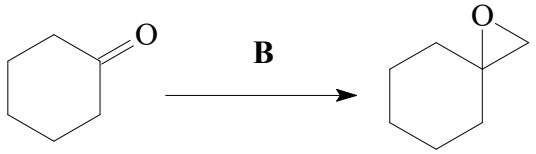
	Answer any ONE of the following	**(1 x 20 = 20)**
14	(a) Discuss the mechanism and limitations of Friedel-Crafts acylation.	(8)
	(b) Explain the formation of major and minor product/s of the elimination of menthyl chloride and neomenthyl chloride.	(6)
	(c) Predict the product and give the mechanism of the following reactions.	(6)

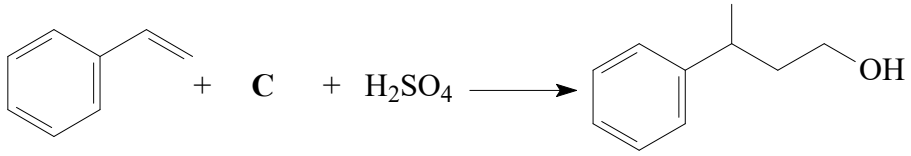
(i) 

(ii) 

15	(a) 'The effect of attacking nucleophile in S_N1 reaction kinetics is negligible.' Why?	(4)
	(b) Identify A, B and C in the following reactions and justify your answer with suitable mechanism.	

(i) **A** + excess HCHO $\xrightarrow{NaOH}$  + HCOONa

(ii) 

(iii) 

(4 + 4 + 4)

(c) Discuss the electrophilic and nucleophilic substitution positions in the imidazole derivatives using suitable examples. (4)
