PSG COLLEGE OF ARTS & SCIENCE (AUTONOMOUS)

MSc DEGREE EXAMINATION MAY 2018

(Second Semester)

Branch - CHEMISTRY

ORGANIC CHEMISTRY - II

Time: Three Hours

Maximum: 75 Marks

Answer **ALL** guestions

ALL questions carry EQUAL marks

 $(5 \times 15 = 75)$

1 a Discuss the mechanism of the given reaction:

- b Why is it necessary to use more than one mole of the catalyst $(A \ell Cl_3)$ per mole of the reagent? (3+2)
- c Predict the mechanism for the given reaction

- d In the preparation of enamine why is it necessary to remove water from the reaction mixture?
- e Why is cyclic amine generally used as the secondary amine in the enamine synthesis?
- f How is water eliminated? (4+2+2+2)

OR

- g Halogens are ring deactivators but o, p directors. Explain. (3)
- h Why is nitration with acetyl nitrate accelerated by adding fluoroboric acid but retarded by adding hydrochloric acid? (3)
- i Benzenediazonium chloride does not couple with anisole whereas 2, 6 dinitro benzene diazonium chloride does? Give reason. (3)
- j Discuss the effect of solvent on SE^1 and SE^2 reactions. (4)
- k Distinguish between singlet and triplet carbenes. (2)
- 2 a Write E1cB mechanism. Why is this mechanism designated as E1cB?
 Which substrates are very prone to react by this mechanism? Illustrate with suitable example.
 - b Neomenthyl chloride in the presence of base undergoes elimination faster than menthyl chloride by 200 times. Explain. (3)
 - c 2-phenyl ethyl bromide undergoes E2 elimination about 10 times as fast as 1 phenyl ethyl bromide. Account for this difference. (3)

2		Cont	
	d	Illustrate Birch reduction with suitable mechanism. OR	(3)
	e	Illustrate Hofmann and Saytzeff rules with suitable example.	(6)
	f	Discuss the synthetic utility of chromic acid and SeO ₂ in organic synthesis.	(6)
	g	Illustrate any one pyrolytic elimination with suitable example.	(3)
3	a	Explain the difference in orientation in the addition of HBr to 1-butene with and without the presence of peroxide.	(4)
	b	Illustrate Michael addition reactions with suitable mechanism.	(4)
•	C.	What is hydroboration? Illustrate with suitable example.	(3)
	d	What is Wittig reaction? Illustrate with suitable mechanism.	(4)
	e	OR Discuss the reactivity of double and triple bonds towards electrophilic substitution.	(5)
	f	Identify the product and predict the mechanism for the following reactions:	
		(i) $2C_6H_5CHO \xrightarrow{:CN} \text{product}$ KCN $COOC_2H_5$ ii) $CH_3CHO + H_2C \xrightarrow{Piperidine} \text{product.}$	(8)
	g	Claisen condensation is intra molecular rearrangement. Justify this statement with suitable example.	(2)
4	a	Discuss the uses of the following reagents in protein chemistry: (i) carbobenzyloxy chloride (ii) p-nitrophenylester (iii) ethylchloroformate	(9)
	b	Illustrate solid phase peptide synthesis with suitable example.	(4).
	c	What are nucleotides?	(2)
	d	OR Distinguish between RNA and DNA.	(3)
	e	How are N-terminal and C-terminal amino acids protected? illustrate with suitable example.	(6)
	f	What are the factors influencing enzyme action?	(3)
	g	Distinguish between enzyme and coenzyme. Cont	(3)

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8 L	n		

a	What are crown ethers? How is dibenzo $-18 - \text{crown} - 6$ synthesised? Discuss the applications of crown ethers in exidation, substitution and elimination reactions.	(8)
b	What is Wilkinson's catalyst? How is it useful in oxidation decarboxylation and angular methylation reactions?	(5)
c	Sodium borohydride is mild reducing agent than lithium aluminium hydride. Comment on it. OR	(2)
d	Discuss the method of preparation and any two synthetic applications of the following reagents:	
	(i) 1, 3 - dithiane (ii) Gilman's reagent	(8)
ė	Discuss the use of ozone in elucidating the structure of alkenes.	(3)
f	Why does 1 – chlorooctane fail to undergo nucleophilic substitution by cyanide in the absence of PTC? What is the role of PTC in effecting the reaction?	(4)
	Z-Z-Z END	