LOYOLA COLLEGE (AUTONOMOUS), CHENNAI – 600 034

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

SECOND SEMESTER – **APRIL 2019**

CH 2819– ORGANIC REACTION MECHANISMS & HETEROCYCLICS

Date: 03-04-2019 Dept. No. Max. : 100 Marks

Time: 01:00-04:00

(4 ×10 = 40)

1a. Why is cyclobutenyl cation homoaromatic?

b. Derive Hammett equation. Explain its limitation (6+4)

2. Write the mechanism of Friedel-Crafts alkylation and acylation of phenol.

3a. Neopentyl halide is very un-reactive towards S_N2 reaction. Explain why?

b. Discuss the mechanism and stereochemistry of S_E1 reaction. (6+4)

4a. Write Swain-Scott equation and mention the terms involved in it.

b. Explain single electron transfer (SET) mechanism with an example. (7+3)

5. Write the mechanism of von Richter rearrangement and explain its importance in determining a reaction mechanism.

6a. State and explain Saytzeff's rule with suitable example.

b. Give an example for 1,3-elimination reaction. (4+6)

7a. Explain the mechanism of Cope reaction with suitable example.

b. Explain the *syn*-&*anti*- elimination reactions with a suitable example for each. (6+4)

8. Give an example for Norrish type I & II reactions. Explain its mechanism.

PART-B

Answer *any THREE* questions. **(3× 20 = 60)**

9a. Discuss the orientation and reactivity of nitrobenzene

b. Explain the mechanism of Stark-enamine reaction.

c. Arrange the following alkenes in their increasing order of reactivity towards the electrophilic addition reaction and justify your answer. (10+5+5)

$Cl_2CHCH=CH_2$, $CH_3CH=CH_2$, $ClCH_2CH=CH_2$, $Cl_3CCH=CH_2$

10a. Explain the Ipso substitution reaction with an example.

b. Discuss the orientation and reactivity of E2 reaction with an example. (10+10)

11a. Explain the benzyne mechanism with suitable examples.

b. Discuss various factors affecting the rate of aliphatic nucleophilic substitution reactions.

c. Explain ion pair mechanism with suitable example. (6+8+6)

12a. Discuss the mechanism and evidences of E1cB reaction.

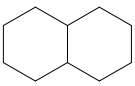
b. List the factors affecting the E1 reaction. Explain. (10+10)

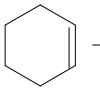
13. Predict the product and suggest the mechanism for the following free-radical reactions.

(i) Isobutane $\xrightarrow[250\text{-}400\ ^\circ C]{Cl_2}$?

(ii) Isobutane $\xrightarrow[h\nu\ ,\ 127\ ^\circ C]{Br_2}$?

(iii) n–Butane $\xrightarrow[25\ ^\circ C]{Cl_2}$?

(iv)  $\xrightarrow{O_2}$?

(v)  $\xrightarrow{O_2}$?

14a. Write the synthetic scheme of Fischer indole synthesis.

b. Give the Baeyer's synthesis of uric acid from urea. (10+10)

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