



**LOYOLA COLLEGE (AUTONOMOUS), CHENNAI – 600 034**

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

**SECOND SEMESTER – APRIL 2014**

**CH 2814 - ORGANIC SUBSTITUTION, ADDITION & ELIMINATION RXNS**

Date : 28/03/2014

Dept. No.

Max. : 100 Marks

Time : 09:00-12:00

**Part-A**

**Answer all the questions. Each carries two marks.**

1. What is homoaromaticity? Give example.
2. Predict the kinetic isotope effect of nitration reaction of tritiated benzene and benzene.
3. 'The effect of attacking nucleophile in  $S_N1$  reaction kinetics is negligible.' Why?
4. What is Grunwald-Winstein relationship?
5. What are *syn*-eliminations? Mention their stereoelectronic requirements?
6. State and explain Saytzeff rule with an example.
7. Predict the product for the reaction between 3,3,3-trichloro-1-propene and bromine in presence of peroxide.
8. Give the number of ESR spectrum for triphenyl methyl radical.
9. Free radical addition of HBr to 1-bromocyclohexene gives only *cis*-isomer and not *trans*-isomer. Justify.
10. Addition of bromine molecule to ethylene in methanol is retarded by the addition of KBr. Why?

**Part-B**

**Answer any eight questions. Each carries five marks.**

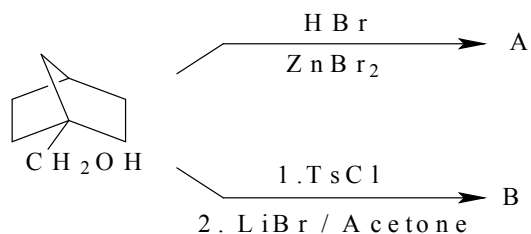
11. What is partial rate factor? Explain the calculation of partial rate factor for any one aromatic electrophilic substitution reaction.
12. Explain the mechanism of Stork-enamine reaction.
13. The  $S_E1$  reaction of an optically active substrate on deuteration in alkaline medium gives racemic mixture. Justify.
14. Which of the following undergoes solvolysis more readily  $(C_6H_5)_2CHBr$  or  $(CH_3)_3CBr$ ? Justify your answer.
15. Explain ion pair mechanism with evidences.
16. Explain von Richter rearrangement with mechanism.
17. What is Hofmann elimination reaction? Explain with mechanism.
18. Discuss the various factors which affect the extent of  $E_1$  and  $E_2$  eliminations.
19. What are the characteristics of free radical reactions?
20. How are long-lived free radicals detected by Gomberg method?
21. Addition of carbenes to unsymmetrical olefin is non-stereospecific in gas phase. Explain.
22. Why is peroxide effect not observed in the addition of HCl to unsymmetrical olefin?

**Part-C**

**Answer any four questions. Each carries ten marks.**

- 23a. Derive the Hammett-Brown equation for aromatic electrophilic substitution. Why is it not applicable for *ortho*-substitution?
- b. Explain the mechanism of the following aliphatic electrophilic reactions with suitable example: (i) insertion by nitrene and (ii) sulphenylation.

- 24a. Give the mechanism of nitrosation and diazonium coupling reactions.  
 b. Explain the *ipso*-substitution reaction with example.
25. Explain the following with evidences: (a) benzyne mechanism and (b) Bucherer reaction.
- 26a. What is Cope reaction? Discuss the mechanism and stereochemistry.  
 b. Prove that the E2 reaction of erythro-1-bromo-1,2-diphenyl propane is stereospecific.
- 27a. Explain the Norrish type I and II reaction mechanism with suitable examples.  
 b. Predict the product of the reaction and justify your answer.



- 28a. Isobutylene oxide reacts with methanol in acidic medium and gives primary alcohol as the major product, whereas in basic medium gives tertiary alcohol as the major product. Explain.  
 b. Explain Sommelet-Hauser rearrangement with mechanism.

\*\*\*\*\*