



LOYOLA COLLEGE (AUTONOMOUS), CHENNAI – 600 034

M.Sc. DEGREE EXAMINATION – CHEMISTRY

SECOND SEMESTER – APRIL 2014

CH 2819 - ORGANIC REACTION MECHANISMS & HETEROCYCLICS

Date : 28/03/2014

Dept. No.

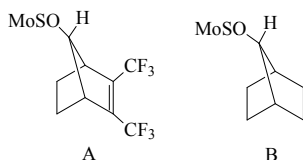
Max. : 100 Marks

Time : 09:00-12:00

Part-A

Answer all the questions. Each carries two marks.

1. Arrange the following substrates in their increasing order of reactivity towards aromatic electrophilic substitution reaction: nitrobenzene, benzene, phenol, toluene, and bromo benzene.
2. Define partial rate factor.
3. What is Stork-Enamine reaction? Mention its advantages.
4. Write any two evidences for E1 reaction.
5. Illustrate *syn*-elimination with an example.
6. Write Swain-Scott equation and mention the terms involved in it.
7. Which of the following will undergo solvolysis very readily and why?



8. Which of the following reacts more readily towards the bromination reaction, styrene or phenyl acetylene? Justify your answer.
9. Give the mechanism of Sommelet-Hauser rearrangement.
10. Arrange the following according to their order of reactivity towards substitution reaction: $\text{CH}_2=\text{CH}-\text{CH}_2-\text{Cl}$, $\text{CH}_2=\text{CH}-\text{Cl}$, and $\text{CH}_2=\text{C}=\text{CHCl}$.

Part-B

Answer any eight questions. Each carries five marks.

11. Account for the following observations:
(a) Mono nitration of aniline gives the *m*-product.
(b) Benzoic acid is meta directing in aqueous or acidic solutions but it is *o*- and *p*-directing in the presence of a base.
12. What are σ - and π -complexes in aromatic electrophilic substitution reaction? Give evidences in favour of their formation.
13. Predict the mechanism of (a) aliphatic diazonium coupling and (b) acylation of olefins.
14. Discuss in brief the factors influencing E1 and E2 reactions.
15. What are free radicals? How are they generated? Mention their important characteristics.
- 16a. Write the mechanism of nitration of benzene.
b. Why is 2,2'-dimethyl biphenyl more difficult to nitrate than biphenyl?
17. Explain the mechanism of Bucherer reaction with evidences.
18. Which of the following undergoes solvolysis very readily, diphenylmethyl bromide or *t*-butyl bromide? Justify your answer.
19. Explain ion-pair mechanism with evidences.
20. Predict the product formed by the addition of carbenes to *trans*-2-butene in gaseous and liquid phases.

21. Write Bayer's synthesis of uric acid from urea.
22. Give any one method to synthesis coumarins.

Part-C

Answer any four questions. Each carries ten marks.

23. Discuss the S_{E2} and S_{Ei} mechanisms of aliphatic electrophilic substitution reactions with evidences.
- 24a. Explain why 3-bromopropanol undergoes base catalyzed dehydrobromination faster than 2-bromopropanol?
b. Discuss the various limitations of Friedel-Crafts alkylation of benzene. (5+5)
- 25a. Describe the nonaromatic behavior of [14]-annulene.
b. Explain the role of desulfonation process in the conversion of aniline to *o*-nitroaniline.
- 26a. Discuss single electron transfer (SET) mechanism with an example.
b. Explain von Richter rearrangement with mechanism. (5+5)
- 27a. Give the evidences for the *syn*-, *anti*-, and nonstereoselective electrophilic addition of olefins.
b. Give the mechanism of Simon-Smith reaction. (5+5)
- 28a. Discuss the electrophilic substitution position of isoquinoline and indole.
b. Predict the product and give the reactions for the following
(i) nitration of *p*-fluoroanisole, (ii) chlorination of phthalic acid, and (iii) bromination of *p*-chlorobenzoic acid. (4+6)
