LOYOLA COLLEGE (AUTONOMOUS), CHENNAI – 600 034

M.Sc. DEGREE EXAMINATION - **CHEMISTRY**

SECOND SEMESTER – **APRIL 2013**

CH 2814/2808 - ORGANIC SUBSTITUTION, ADDITION & ELIMINATION RXNS

Date : 26/04/2013 Dept. No. Max. : 100 Marks

Time : 9:00 - 12:00

PART-A

Answer ***ALL*** questions. (10 x 2 = 20)

01. Explain aromaticity of the following with their structure?

(i) Tropylium anion (ii) Tropyliumcation

02. Calculate the partial rate factor for the reaction of nitration of toluene?

03. What is Swain-Scott relationship?

04. Write the mechanism of Bucherer reaction.

05. Arrange the following according to their order of reactivity towards substitution reaction.

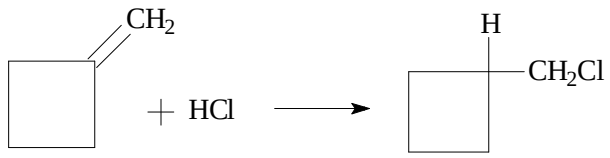
$(CH_3)_3C$-Cl ,CH_2=CH-Cl, CH_2=CH-CH_2-Cl , CH_2=C=CHCl

06. Predict the products for the reaction between *m*-dichlorobenzene with KNH_2 in liq. NH_3 and mention the intermediate involved in it.

07. What is Cope reaction? Give an example.

08. How would you identify the formation of triphenylmethyl radical?

09. Account for the following observation:

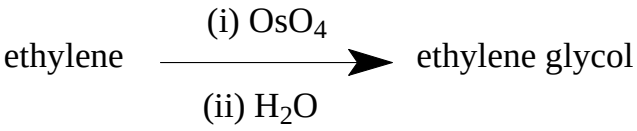


10. How would you convert 3-hexene to 1-hexene?

PART-B

Answer ***ANY EIGHT*** questions. (8 x5 = 40)

11. Show the linear free energy relationship in aromatic electrophilic substitution reaction and explain its importance.
12. Write the mechanism of the following ArSE reaction with the formation of electrophile.
    (i) Nitrosation (ii) Acylation
13. Explain theS_E2(back) and S_E2(forward)reaction with an example.
14. Explain ion-pair mechanism with evidences.
15. Explain von Richter rearrangement with mechanism.
16. State and explainSaytzeff and Hoffmann elimination reactions with suitable example.
17. Discuss in brief the mechanism and stereochemistry of E2 elimination reaction.
18. Give the mechanism of the nucleophilic substitution reaction using any two ambient necleophiles.
19. Explain the free radical mechanism of chlorination of neopentane and justify your answer.
20. What is meant by neighbouring group participation? Explain this concept in free radical substitution with a suitable example.
21. Explain the mechanism of a reaction between propene with borane.
22. Give the mechanism for the following conversion:



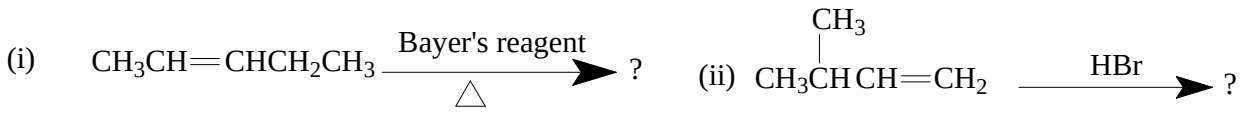
PART-C

Answer ***ANY FOUR*** questions. (4 x10 = 40)

23. a) Discuss the orientation and reactivity of chlorination of nitrobenzene.
    b) Explain the mechanism of the following aliphatic electrophilic reactions with suitable example:

(i) Stark-enamine reaction (ii) sulphenylation

24. a) Explain the Ipso substitution reaction with example.
    b) Hammett equation is not applicable for aliphatic &*ortho*-substitution. Why?
25. Explain the following with examples.
    a) Benzyne mechanism b) Sommelet-Hauser rearrangement
26. a) Prove that the E2 reaction of erythro-1-bromo-1,2-diphenyl propane is stereospecific.
    b) Explain Hofmann degradation reaction with an example.
27. (a) Explain the Norrish type I & II reaction mechanism with suitable example.
    (b) Write and explain the mechanism of free radical substitution in aromatic substrate.
28. Predict the product of the following reaction and explain their mechanism:



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