

LOYOLA COLLEGE (AUTONOMOUS), CHENNAI – 600 034

M.Sc. DEGREE EXAMINATION – CHEMISTRY

SECOND SEMESTER – APRIL 2010

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

Date & Time: 16/04/2010 / 1:00 - 4:00 Dept. No.

Max. : 100 Marks

PART-A

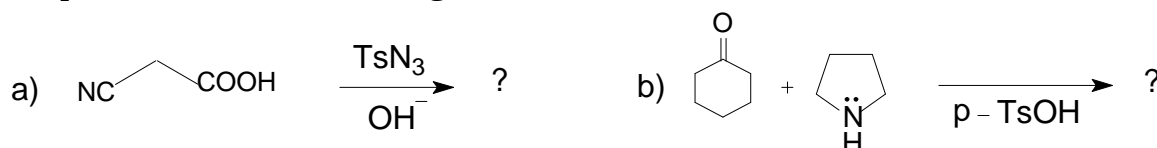
Answer **all** questions.

(10 x 2 = 20)

01. Which of the following compounds are aromatic?



02. Give the products of the following reactions



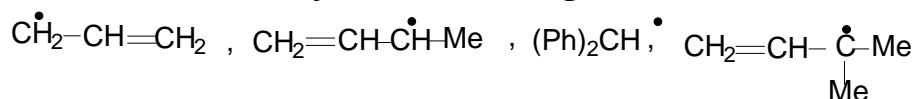
03. 'On treating fluorobenzene with deuterated amide ion, the unreacted starting material at any time contains deuterium'. Why?

04. 'Basic hydrolysis of α -bromopropionate ion with conc. base gives inverted product while dilute base gives retention product'. Why?

05. What is 'product spread' in allylic nucleophilic substitution reactions? Explain.

06. What happens when isobutyl acetate is strongly heated?

07. Write the order of stability of the following free-radicals;



08. Mention the advantages and disadvantages of the Paneth mirror removal technique.

09. $\text{F}_2\text{C=CF}_2$ does not undergo electrophilic addition reaction with HBr. Why?

10. 'Anti Markownikov's rule is followed only for the addition of HBr to an unsymmetrical alkene and not with other hydrogen halides'. Why?

PART-B

Answer **any eight** questions.

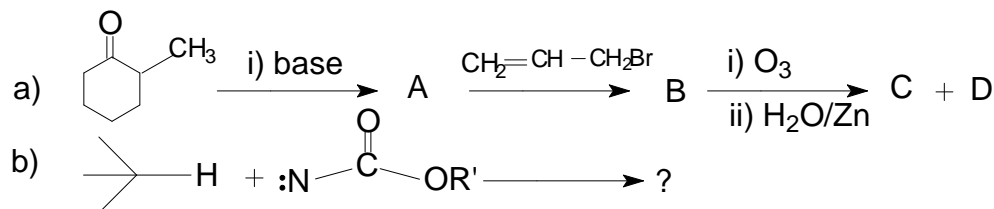
(8 x 5 = 40)

11. a) Write the arenium ion mechanism? (2)

b) Explain the ipso attack in the electrophilic aromatic substitution reaction. (3)

12. Explain the stereochemistry of $\text{S}_{\text{E}}2$ reaction mechanism. (5)

13. Identify the products in the following reactions. (4+1)



14. What are ambident nucleophiles? Explain with suitable examples.

15. 'Trans-2-acetoxycyclohexyl brosylate on acetolysis using glacial acetic acid gives only trans product'. Explain.

16. Explain the mechanism of Smiles rearrangement with a suitable example.

17. 'The ratio of cis-2-olefin to trans-2-olefin obtained from the unimolecular elimination reaction of Et-CHMe-OBs is about twice that obtained from i-Bu-CHMe-OBs under comparable conditions'. Explain.

18. How does selenide elimination help in the synthesis of α,β -unsaturated ketones? Explain the sequence of the reaction.
19. How will you produce a short-lived free radical from tetramethyl lead and explain with a method to detect them?
20. The hydrogen and methyl group do not migrate in the free radical rearrangement reactions. Explain with three evidences.
21. Explain the orientation and reactivity of addition reactions to C-C multiple bonds.
22. Explain the mechanism of hydroboration-oxidation reaction with 1-butene.

PART-C

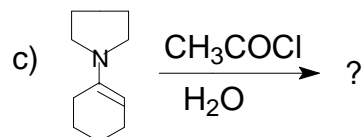
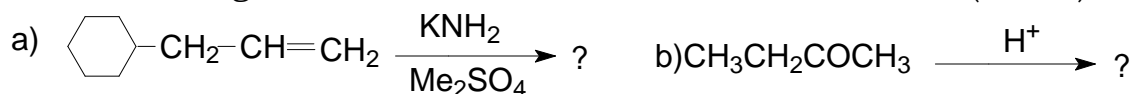
Answer **any four** questions.

(4 x 10 = 40)

- 23.(a) Derive the Hammett and Taft equation. Explain their applications and Limitations in the ArSE reactions. (8)

(b) What is partial rate factor? (2)

24. Explain the following reactions with mechanism. (4+2+4)



25. Explain the following :

a) The relative rates of solvolysis of tert-BuBr in 60% ethanol is 2.41×10^4 while in water is 1.2×10^6 .

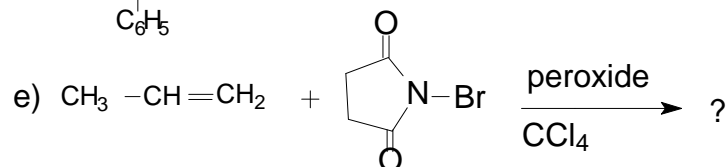
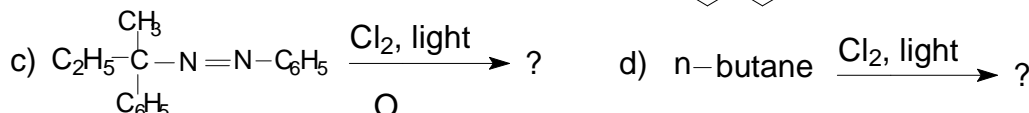
b) $\text{S}_{\text{N}}1$ rates are greatly increased when there is a double bond in the β -position.

c) The rates of hydrolysis of alkyl bromides (0.1M) in 0.01M NaOH are in the order of t-BuBr > MeBr > EtBr > i-PrBr.

- 26a) How does the stereochemistry of the products differ on the hydroxylation of 2-pentene using (1) alkaline KMnO_4 and (2) perperzoic acid?

b) Explain Bucherer reaction with mechanism taking β -naphthol as an example.

27. Predict the product of the following reactions. (5 x 2 = 10)



- 28.(a) How does Cyclopropane undergo electrophilic addition reaction like alkenes? Justify your answer. (4)

(b) Identify the products obtained when erythro and threo isomers of 1-acetoxy-2-deutero-1,2-diphenylethane are subjected to pyrolysis. Justify your answer. (6)

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