LOYOLA COLLEGE (AUTONOMOUS), CHENNAI – 600 034

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

SECOND SEMESTER – **APRIL 2024**

PCH 2501 – ORGANIC REACTION MECHANISM AND HETEROCYCLIC COMPOUNDS

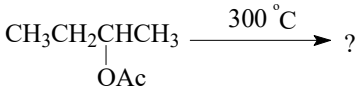
Date: 23-04-2024 Dept. No. Max. : 100 Marks

Time: 09:00 AM - 12:00 NOON

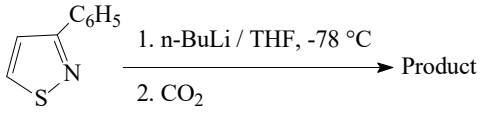
Part-A

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

1. How does cyclooctatetraene exhibit homo-aromaticity?
2. Write the mechanism of S_Ei reaction.
3. Predict the product with mechanism of the following reaction:



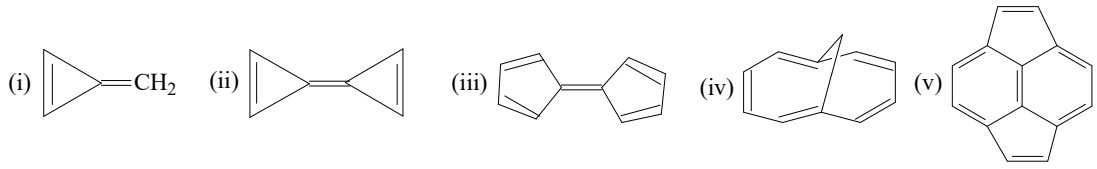
4. How would you detect the following free-radicals?
   (i) Triphenylmethyl radical (ii) Ethyl radical
5. Arrange the following alkenes in their increasing order of reactivity towards electrophilic addition reaction and justify your answer.
   $Cl_2CHCH=CH_2$, $CH_3CH=CH_2$, $ClCH_2CH=CH_2$, $Cl_3CCH=CH_2$
6. Write Swain-Scott equation and mention the terms involved in it.
7. Why is neopentyl halide very un-reactive towards nucleophilic substitution?
8. Which among the following will undergo electrophilic addition? Account for your choice.
   $HC_2=CHCN$ and $CH_2=CHCH_2CH_3$
9. Write the tautomeric structures of 5-methylimidazole.
10. Identify the product of the following reaction.



Part-B

Answer any FOUR questions. **(4 × 10 = 40)**

11. Apply the conditions for aromaticity and predict the aromaticity of the following compounds.



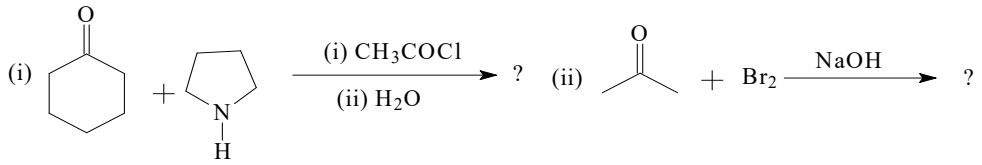
12. Illustrate the mechanism and stereochemistry of S_E1 & S_E2 reaction with examples.
13. Explain the mechanism, stereochemistry, evidences, orientation and reactivity of E1 reaction with a suitable example.
14. Describe the following methods of formation of long-lived and short-lived free-radicals.
    (i) Gomberg method (ii) Paneeth mirror-removal technique (5 + 5)
15. (a) "CH_2=CH-CH_2-Br undergoes S_N2 reaction slightly more rapidly than ethyl bromide" Why? (5)
    (b) Reactions of *o*- & *m*-dichlorobenzene with KNH_2 in liq. NH_3 forms identical product. Justify. (5)
16. (a) "Addition of carbene to unsymmetrical olefin is stereospecific in liquid phase". Explain. (5)
    (b) What are the conditions for a compound to undergo Michael 1,2- and 1,4-addition reactions? (5)
17. Explain the following with evidences.
    i) Benzyne mechanism ii) Bucherer reaction (5 + 5)
18. Write any one method of synthesis for pyridazine and pyrimidine. (5 + 5)

Part-C

Answer any TWO questions. **(2 × 20 = 40)**

19. (a) Why does 1-isopropyl-4-methylbenzene give some product of 'ipso' substitution, while 1,4-dimethylbenzene produces only substitution product? Explain. (6)

(b) Identify the product/s and explain the mechanism of the following reactions. (8)



(c) Write the arenium-ion mechanism with any one evidence. (6)

20. (a) Discuss the mechanism, stereochemistry, orientation and reactivity of an E2 reaction with suitable examples. (10)

(b) Sketch the mechanisms of *syn*- & *anti*-eliminations with examples. (4)

(c) Illustrate the mechanism of Norrish type-I & II reactions with example. (6)

21. (a) Explain Ion Pair mechanism with evidences. (7)

(b) Which among the following will undergo solvolysis more readily? Justify.
$(C_6H_5)_2CHBr$ or $(CH_3)_3CBr$ (6)

(c) Explain single electron transfer (SET) mechanism with an example. (7)

22. (a) Explain von Ritcher rearrangement with mechanism. (5)

(b) How are 1,3-oxazole and thiazoles synthesised by Hantzsch and Robinson-Gabriel syntheses? Discuss their substitution position in the electrophilic substitution reactions. (15)
