LOYOLA COLLEGE (AUTONOMOUS), CHENNAI – 600 034

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

FIRST SEMESTER – NOVEMBER 2017

17PCH1MC01 - ORGANIC REACTION MECHANISM AND STEREOCHEMISTRY

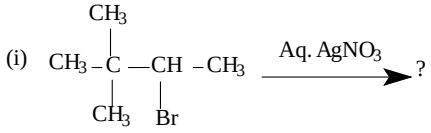
Date: 02-11-2017 Dept. No. Max. : 100 Marks

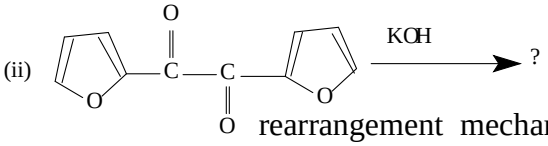
Time: 01:00-04:00

Part-A

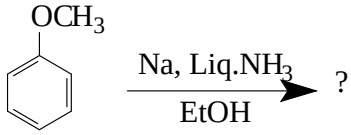
Answer ALL questions. **(10 × 2= 20)**

1. What are the conditions for a thermodynamically controlled chemical reaction?
2. Draw the potential energy diagram for the nucleophilic substitution of a two step reaction. Label ΔG°, $\Delta G^{\neq}$, transition states and intermediates.
3. Predict the product in the following reaction.



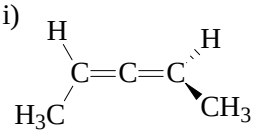


4. Write a rearrangement mechanism which involves ring contraction.
5. Predict the product of the following reaction.

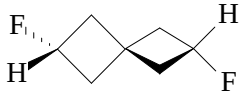


6. What is Bouveault-Blanc reduction?
7. Compare the conformational stabilities of diastereomers using general substituents.
8. The specific rotation of *R*(+)-glyceraldehyde is + 8.7°. If the observed specific rotation of the mixture of *R*-glyceraldehyde and *S*-glyceraldehyde is + 1.4°, what is the percentage of *R*-isomer in the mixture?
9. What is second order asymmetric transformation?
10. Assign R/S for the following compounds.

i)



ii)



Part-B

Answer any EIGHT questions. **(8 × 5= 40)**

11. State and explain the Hammond postulate with mechanism and draw the potential energy diagram for the reaction of bromination of alkanes.

12a. How is isotopic labeling study helpful to determine the mechanism of acid catalysed hydrolysis of an ester? (3)

b. How will you detect the formation of benzyne intermediate? (2)

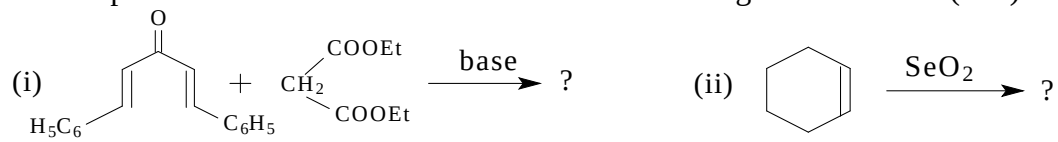
13. Derive the Hammett equation to correlate the substituent and reaction constants.

14a. How would you convert 1,7,7'-trimethyl bicycle[2,2,$1^{1,4}$]heptan-2-ol into 2,2'- dimethyl-3-methylidene bicyclo [2,2,$1^{1,4}$] heptane? (3)

b. Write the mechanism of benzidine rearrangement. (2)

15. Explain the mechanism of Fischer-indole synthesis.

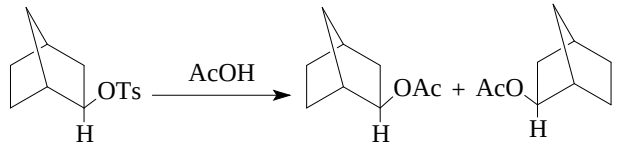
16. Predict the product and write the mechanism of the following reactions. (3+2)



17. Compare the mechanisms of Wolff-Kishner and Clemmensen's reduction with suitable examples. (3+2)

18. Explain the stereochemistry of the acetolysis reactions of 2-phenyl-3-pentyl tosylate and 3-phenyl-2-pentyl tosylate in acetic acid.

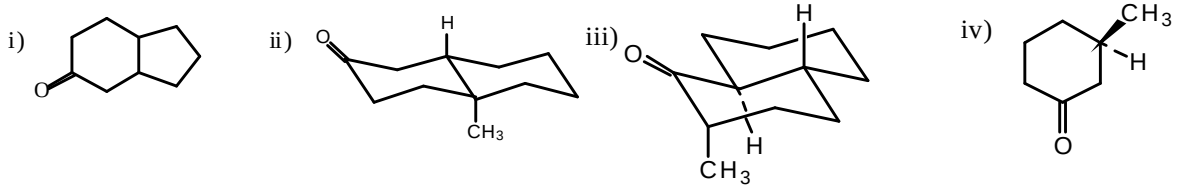
19. Explain the following observations with suitable mechanism:



20. Write a note on absolute asymmetric synthesis with a suitable example.

21. Explain the chemical method of racemisation by anion intermediate formation with a suitable example.

22. Predict the cotton effect for the following compounds.



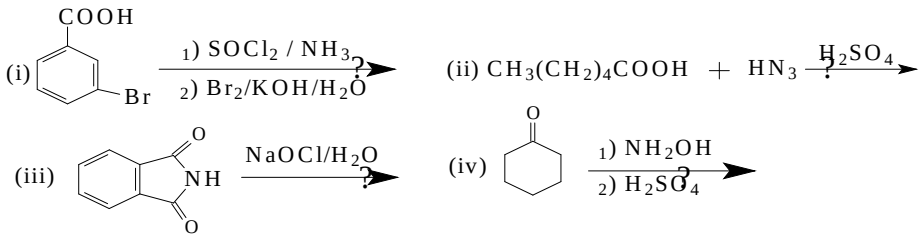
Part-C

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

23a. Explain the importance of kinetic isotope effect (KIE), primary KIE, secondary KIE, inverse KIE and solvent KIE in determining the reaction mechanism. (5)

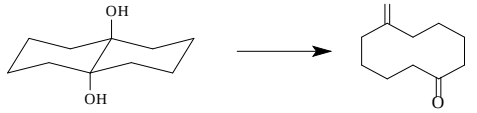
b. The rate law of benzoin condensation reaction is $-d[C_6H_5CHO]/dt = k[C_6H_5CHO]^2 [CN^-]$. Explain the mechanistic implications of the rate law in this reaction. (5)

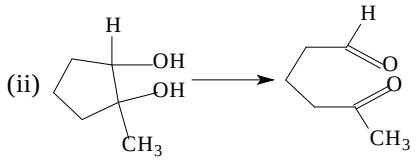
24a. Draw the structure of the major product obtained from each of the following reactions. (4)



b. Explain the mechanism of ortho-Claisen and *para*-Claisen rearrangement reactions. (6)

25a. Suggest a mechanism for the following conversions using suitable oxidizing agents. (6)

(i) 

(ii) 

b. Explain the mechanism of any two synthetic applications of DDQ and chloranil. (4)

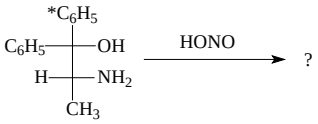
26a. Compare the selectivity of LAH and NBH with an example for each. (4)

b. Explain the following with a suitable example for each. (2+2+2)

i) Absolute asymmetric synthesis ii) Bredt's rule iii) Epimerisation

27a. Discuss the conformation and stabilities of 1,2 and 1,3 –diethyl cyclohexane. (4)

b. Apply Curtin-Hammett principle and discuss the stereochemistry of the following reaction. (6)



28. Discuss the stereochemistry of the following.

i) Pyrolysis reaction of *cis*- and *trans*-2-phenylcyclohexylxanthates.

ii) Reaction of erythro-3-bromo-2-butanol with HBr

iii) 2,3-pentadiene does not possess any chiral carbon but is resolvable into enantiomers. (4+3+3)

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