(Pages: 2)

Name:	 	
Reg. No	 	

FIRST SEMESTER M.Sc. DEGREE EXAMINATION, NOVEMBER 2019 (CUCSS PG)

CC19P CHE1 C03 – STRUCTURE AND REACTIVITY OF ORGANIC COMPOUNDS

(Chemistry)

(2019 Admission Regular)

Time: Three Hours

Maximum: 30 Weightage

Section A

Answer any *eight* questions. Each question carries 1 weightage.

- 1. Comment on the stability of hydrates of glyoxal, chloral and ninhydrin.
- 2. Explain Bredt's rule with suitable example.
- 3. Illustrating examples, explain thermodynamic control and kinetic control of reactions.
- 4. State and explain Hammond's postulate.
- 5. Giving examples, briefly explain any two factors that affect conformational stability of molecules.
- 6. Draw and explain the most stable conformation of *cis*-1-*tert*-butyl-4-methylcyclohexane.
- 7. The bridgehead adamantyl tosylate does undergo S_N1 reaction extremely slowly and it does not undergo S_N2 reaction. Validate the statement.
- 8. Assign the *E* or *Z* notation for the following compounds.

(i) Me Br (ii)
$$(H_3C)_3C$$
 Ph
H Et H NMe₂

- 9. Giving examples, differentiate stereoselective and stereospecific reactions.
- 10. Predict the product of the following reaction with stereochemistry.

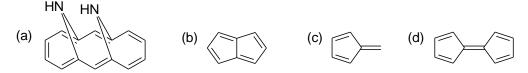
OH
$$\frac{\text{Ti}(\text{O-iPr})_4, (-)\text{DET, TBHP}}{\text{CH}_2\text{Cl}_2, -20^{\circ}\text{C}, 16 \text{ hours}} ?$$

(8 x 1= 8 Weightage)

Section **B**

Answer any *six* questions. Each question carries 2 weightage.

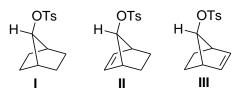
 Classify the following compounds as aromatic, *anti*-aromatic or non-aromatic. Rationalize your answer.



- 12. Write a brief note on different methods of resolution.
- 13. State Curtin-Hammett principle. How do you apply this principle in the dehydrochlorination of chlorocyclohexane.

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14. Arrange the following compounds **I**, **II** and **III** in the increasing order of their rate of reaction on acetolysis. Find out the product with stereochemistry in each case and give reason.



- 15. Explain dehydrohalogination of *erythro-* and *threo-*bromo-1,2-diphenylpropane.
- 16. Explain the asymmetric hydroboration reaction using IPCBH₂ and IPC₂BH.
- 17. Describe optical isomerism in: (i) Biphenyls; (ii) Allenes.
- 18. Draw the structure of Felkin-Ahn model for the LiAlH₄ reduction of **A** and predict the major and minor product.



(6 x 2= 12 Weightage)

Section C

Answer any *two* questions. Each question carries 5 weightage.

19. (a) Emphasizing the significances of Hammett parameters, explain Hammett equation.

(2wt.)

(b) What are linear free energy relationships? Derive Hammett linear free energy relationship.

(1 wt.)

- (c) Explain Taft equation and its advantages over Hammett equation. (2 wt.)
- 20. Illustrating examples, explain aromaticity, *anti*-aromaticity, *homo*-aromaticity and *hetero*-aromaticity.
- 21. Using conformational arguments, compare and explain the course and rate of reactions in:
 - (i) Esterification of methanol, isomenthol, neomenthol, and neoisomenthol. (2 wt.)
 - (ii) Eliminations of *cis* and *trans* isomers of 4-*t*-butylcyclohexyl tosylate and phenylcyclohexanol. (2 wt.)
 - (iii)Oxidation of the conformers of cyclohexanols by chromic acid. (1 wt.)
- 22. With appropriate examples, illustrate the use of chiral pool, chiral auxiliary, chiral reagent and chiral catalysts in asymmetric synthesis. Mention the merits and demerits in each case.

(2 x 5 = 10 Weightage)
