17P114 (Pages:2) Name: ………………..

Reg. No………………

FIRST SEMESTER M.Sc. DEGREE EXAMINATION, DECEMBER 2017

(Regular/Supplementary/Improvement)

(CUCSS-PG)

CC15P CH1 C03 – STRUCTURE AND REACTIVITY OF ORGANIC COMPOUNDS

(Chemistry)

(2015 Admission onwards)

Time: Three Hours   Maximum:36 Weightage

PART - A

Answer *all* questions. Each question carries 1 weightage.

1. The compound $HS-CH_2-CH_2-CH_2-CH_2-Br$ on solvolysis gave a product which showed only two multiplets of 4 protons each in ^1H-NMR spectrum. Why?

2. Write a note on Marcus equation.

3. Write a note on Hammet acidity function.

4. Write a note on Curtin Hammet principle.

5. Explain why azulene molecule has a fairly high dipole moment of 0.8D.

6. What are mesoionic compounds?

7. Account for the fact that o-nitrophenol has a lower boiling point compared to para isomer.

8. Why tropylium bromide exists as an ionic compound?

9. Give the antiperiplannar, anticlinal, synclinal and synperiplannar conformations of 1,2-dichloroethane using Newman projections

10. Account for the fact that cis-1,3-di-tert-butylcyclohexane exist in chair form and it trans isomer will not.

11. Methyl xanthate esters of menthol give 3-menthol whereas neomenthol gives 2-menthol. Explain

12. Explain Bredt's rule

$(12 \times 1 = 12 \text{ weightage})$

PART -B

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

13. Explain (i) why Hammet equation is a linear free energy relationship (ii) importance of ρ and σ in relation to reactivity of substituted benzene derivative.

14. What are chiral auxiliaries and chiral catalysts?
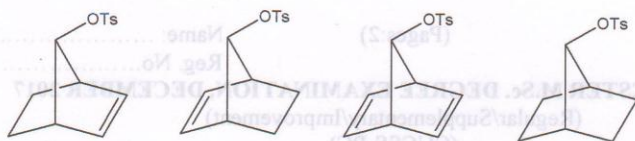
15. Compare the rate of Acetolysis of these compounds with explanation

16. Give chiral pool synthesis of beetle pheromone component (S)-(-)-Ipsenol from (S)-(-) Leucine.

17. Explain with a suitable example following (a) homoaromaticity (b) antiaromaticity

18. Discuss origin of atropisomerism with suitable examples.

19. Explain chemical methods of resolution of racemates through formation of diastereomers.

20. Discuss aromaticity in 8-annulenes

21. Whereas the trans isomer of 1,2-dimethylcyclohexane is more stable than its cis isomer, the cis-1,3-dimethyl cyclohexane is more stable than trans isomer. Explain why?

22. 2,3-dibromobutane has both meso and chiral diastereomer. When the meso diastereomer is boiled in acetone with KI, it affords trans 2-butene. When the chiral diastereomer is treated with in the same way, cis-2-butene is obtained. Which process is faster and explain why.

23. Give the effect of conformation on the course and rate of the reaction in E_1 & E_2 elimination illustrated by (1) menthyl and neomenthyl chloride (ii) benzene hexachloride

24. Give an account of the effect of conformation of dl-dibromostilbene by KI.

$(8 \times 2 = 16$ weightage$)$

PART -C

Answer any *two* questions. Each question carries 4 weightage

25. Write short notes on (i) Sharpless asymmetric dihydroxylation (ii) Zimmermann - Traxler model for diastereoselective aldol reaction.

26. Discuss aromaticity of 4, 10 and 14 annulenes.

27. Discuss the effect of conformation on (i) the stability of dichlorocyclohexanes (ii) the rate of HBr elimination reaction of erythro and threo 1-bromo-1,2-diphenyl propane and (iii) semipinacolone deamination of cis and trans 2-aminocyclohexanols.

28. (a) Explain the stereochemistry involved in Sharpless' asymmetric epoxidation and dihydroxylation

    (b) Explain optical activity in allenes with suitable examples

$(2 \times 4 = 8$ weightage$)$

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