93041   (Pages : 2)   Name.................................

                                       Reg. No. ....

FIRST SEMESTER M.Sc. DEGREE EXAMINATION, DECEMBER 2015

(CUCSS)

Chemistry

CH 1C 03—STRUCTURE AND REACTIVITY OF ORGANIC COMPOUNDS

(2015 Admissions)

rime : Three Hours   Maximum : 36 Weightage

Section A

Answer **all** *questions.*

Each question carries 1 weightage.

1. Explain the bonding in : (a) the P ylide $Ph_3P=CH_2$; and (b) the S ylide $Me_2S=CH_2$.

2. The solvolysis of the acetate of 2-phenylethanol is much faster than the acetate of n-propanol. Why

3. Consider *trans-1* and *cis-1*, 2-dimethylcyclohexanes ; which one is more stable and why ?

4. Account for the observation that the rate of esterification of *trans-* and *cis-*4-t-butylcyclohexane carboxylic acid are different.

5. Compared to its cis-isomer, *trans*-decalin is conformationally biased. Why ? Use stereo diagrams to explain your answer.

6. Draw the projection of the most stable conformer of *meso*-PhCH(Cl)-CH(Cl)Ph and predict the result of its dehalogenation using KI.

7. Plane polarized light passes unaffected through a solution of MeCH=CH-CH=CHMe whereas it is affected when passed through a solution of MeCH=C=CHMe. Why ?

8. Draw the Fischer projection of (2R, 3S)-3-methyl-2-phenylbutanal.

9. Identify and sketch the Re-face of 2-butanone.

10. The C=C bromination of styrene $Ph-CH=CH_2$ can be stereoselective but not stereospecific whereas that of methyl cinnamate Ph-CH=CH-COOMe can be stereoselective as well as stereospecific. Comment.

11. Define chiral auxiliary and cite an example. What are the structural properties and chemical reactivities needed for a good chiral auxiliary ?

12. Write an example for a 1, 2-asymmetric induction. Explain your choice.

                                       (12 x 1 = 12 weightage)

Turn over

Section B

Answer any **eight** *questions.*

Each question carries **2** *weightage.*

13. How many sugar rings are involved in the formation of a β-cyclodextrin molecule ? Which is sugar present and how are these interconnected ? What is the size of its molecular cavity ?

14. With examples, illustrate the effect of hydrogen bonding on the physical and chemical proper· of organic compounds.

15. Explain Hammond postulate regarding the structure of the transition state in relation to free energy. What are its uses ?

16. In the study of two reactions, both involving C-H bond cleavage, one reaction had a kin_ isotoipe effect KIE of 1.20 whereas the other had KIE of 1.02. What can be concluded regard the mechanism of these two reactions on this basis ? Explain.

17. Using suitable projections, discuss the conformations of n-butane. Explain the nomenclature to denote the various conformations as the central C-C bond rotates.

18. Comment on the conformations of ∩ bromocyclohexanone and 2-bromo-4, 4-dimethylcyclohexanone

19. Write a note on conformationally biased molecular systems. Include their applications in answer.

20. Between cis-and *trans* ∩-t-butylcyclohexanol, which one would eliminate water more easily a₁₁ why ? What product(s) would form ?

21. Illustrate how the stability of conformers affect product structure in dehydrochlorination of me and neomenthyl chlorides.

22. State and explain Bredt's rule. What is its structural basis ?

23. Identify all optical isomers of dimethylcyclohexane and draw their most stable chair conforma

24. Using IPC_2BH (di isopinocampheylborane), explain the stereoselective conversion of *trans*-2-bu₁ to predominantly (S) $MeCH_2$-Ch(Me)-OH by hydroboration followed by reaction with H̲Q̲.

(8 x 2 = 16 weightage

Section C

Answer any **two** *questions.*

Each question carries **4** *weightage.*

25. Discuss the aromaticity of annulenes and heteroannulenes. Highlight the structural requirements required for annuleles to exhibit their aromaticity.

26. What are the Hammett's parameters ? Explain what can be learnt from these parameters about mechanism of a reaction and the influence of substituents on it.

27. Explain the origin of atropisomerism and its designation in chiral biphenyls.

28. Write a brief note on asymmetric aldol reaction.

(2 x 4 = 8 weightage)