D 93038 **(Pages : 2)** **Name**

Reg. No.....

FIRST SEMESTER M.Sc. DEGREE EXAMINATION, DECEMBER 2015

(CUCSS)

Chemistry

CH 1C 03—ORGANIC CHEMISTRY—I

(2010-2014 Admissions)

Time : Three Hours Maximum : 36 Weightage

Section A

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

1. Between the two brosylates, $Me_3C–CH_2–CH_2–O–SO_2–C_6H_4–Br–4$ and $Me_2C(Ph)–CH_2–CH_2–O–SO_2–C_6H_4–Br–4$, which will solvolyze faster and why ?
2. Benzyl bromide does not dissolves in water, whereas tropylium bromide does. Why ?
3. Comment on the priority of the following two fairs of groups as per the CIP system :

   (a) [– Ph] and [– C a CH] and (b) [– C ≡ N] and [– CO – NH_2]
4. Write the structures of all isomeric dimethylallenes and denote which one(s) would be optically active. Draw the stereostructre of these optical isomers.
5. Based on Cram's rule, which diastereomer would predominate in the Grignard reaction of PhMgBr with (R) – PhCH(Me) – CHO ? Use projections to explain.
6. Draw the stereostructure of (R,R)-DIOP and identify where Ru would co-ordinate with it. What is the use of such a complex ?
7. Based on conformational arguments, predict the rate of esterification of cis-and trans-4-t-butylcyclohexane-1-carboxylic acids.
8. Consider the di-equitorial conformers of trans-1,2-and 1, 4-dichlorocyclohexanes. Which is less stable and why ? Are these optically active ?
9. What is Prins reaction ?
10. Suppose EtO – CO – $(C1l_2)_3$ – CO – OEt would cyclize upon reaction with sodium ethoxide in dry ethanol, to give, 2-ethoxycarbonylcyclobutan- 1-one, what would be a plausible mechanism ? Which named reaction would this be ?
11. Stobbe condensation is thought to involve a cyclic intermediate. Which one and how does it form and react further ?

Turn over

12. What are the role of radical initiators and quenchers in free radical polymerizations ?

13. Differentiate between primary and secondary structures of proteins.

14. How can copolymers be obtained ?

(14 x 1 = 14 weightage)

Section B

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

15. How are pKa values of organic compounds affected by delocalization of electrons ?

16. Reaction mechanisms can be established by isotope labeling. Explain how.

17. Discuss the stereochemistry of benzaldoxime and acetophenone ketoxime.

18. Write an account of the optical activity of sulfur and nitrogen compounds.

19. Write a note on chiral reagents.

20. What is a chiral pool ? Explain it by using the asymmetric synthesis of benzodiazepines.

21. What is the role of conformation in the hydrolysis of methyl cyclohexylcarboxylic ac. and its substituted derivatives ?

22. Describe the conformations of decalin and sucrose.

23. Explain the need for protecting groups during peptide synthesis. Which are the common amino protection methods used ?

24. Write the mechanism of benzoin condensation. (7 x 2 = 14 weightage)

Section C

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

25. How does conformational factors influence (a) The reaction of methyl magnesium bromide with 2 – phenylpropionaldehyde ; and (b) The thermal elimination reaction of cyclohexyl acetates.

26. Describe the conformations of cyclohexanone, 2 – bromocyclohexanone and 2 – bromo – 4, 4 – dimethylcyclohexanone and cis- and trans – 2, 6 – dibromocyclohexanones.

27. How does Taft equation explain the polar and steric effects in organic reactivity ?

28. Discuss the aromaticity of annulenes and heteroannulenes.

(2 x 4 = 8 weightage)