STELLA MARIS COLLEGE (AUTONOMOUS) CHENNAI - 600 086

(For candidates admitted during the academic year 2008 – 08)

SUBJECT CODE: CH/PC/OC14

M.Sc. DEGREE EXAMINATION, NOVEMBER 2008 **BRANCH IV - CHEMISTRY** FIRST SEMESTER

REG NO.____

COURSE : MAJOR - CORE

: ORGANIC CHEMISTRY **PAPER**

TIME : 30 MINUTES MAX. MARKS: 20

SECTION - A

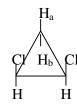
TO BE ANSWERED ON THE QUESTION PAPER ITSELF: (20X1=20)

ANSWER ALL THE QUESTIONS:

I Choose the correct answer:

1. Br
$$C = C = C_1^{1/1}$$
 this allene is

- a) Chiral
- b) achiral
- c) Racemic
- d) meso compound
- 2. In Cis – 1,2-dichloro cylopropane the protons labelled as 'a' and 'b' are

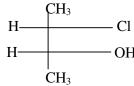


- a) erantiotopic
- b) homotopic
- c) heterotopic d) diastereo topic
- 3. The number of methoxyl groups present in an alkaloid can be estimated by
 - a) Ziesel method

b) Cram's method

c) Zerewitinoff's method

- d) Prelog's method
- Pyrolysis of amine oxide proceeds by the mechanism 4.
 - a) $S_N 2$
- b) E_2
- c) E_i d) $S_N 1$
- 5. The Fischer projection given below is labeled as



- a) Erythro
- b) threo
- c) meso
- d) ±

| 6. | Boat conformation of cyclohexane has a) four pairs of eclipsed bond c) two pairs of eclipsed bond | b) three pairs of eclipsed bond d) one pairs of eclipsed bond | | | |
|------|---|--|--|--|--|
| 7. | The number of chiral centres present in cholesterol molecule is a) 6 b) 7 c) 4 d) 8 | | | | |
| 8. | The structure of Carbanion is a) pyramidalc) square pyramidal | b) planard) trigonal bipyramidal | | | |
| 9. | CI $C = C = C^{1/1/1}CH_3$ $C(CH_3)_3$ is | | | | |
| | a) meso b) disymmetric | c) achiral d) Asymmetric | | | |
| 10. | Trans-Cyclooctene is chiral due to the p a) Chiral Centre b) Chiral axis | resence of c) Chiral plane d) helical structure | | | |
| Fill | in the blanks: | | | | |
| 11. | The configuration of the alkene formed by the elimination of one molar equivalent of HBr from | | | | |
| | H Br. CH3 is | [E/Z]. | | | |
| 12. | The migratory aptitude of aryl group is than alkyl | | | | |
| | group. | | | | |
| 13. | Achiral molecule with one or two proper axis is called | | | | |
| | molecule. | | | | |
| 14. | When in a reaction no bonds to the stereocentre are broken, the reaction proceeds | | | | |
| | with in o | configuration. | | | |
| 15. | Cis and trans 1,4 – disubstituted cyclehexane are | | | | |
| | [chiral/achiral] | | | | |

II

III Answer the following in one or two sentences:

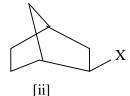
16. Comment on the chirality of the naturally occurring antibiotic mycomycin. The structure is given below.

 $HC = C - C \equiv C - CH = C = CH - CH = CH - CH = CH - CH_2COOH$





[i]



Why [i] is unreactive toward S_N1 and S_N2 reaction whereas [ii] reacts via these mechanisms.

- 18. Compare the basic character of pyrrole and pyridine and explain.
- 19. Predict the order of stability of carbanion.
 Tertiary, primary, methyl, secondary
- 20. Name the reagent and the reaction used to convert Indole to 3-chloroquinoline.

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COURSE : MAJOR - CORE

PAPER : ORGANIC CHEMISTRY

TIME : 2½ HOURS MAX. MARKS : 80

SECTION - B (5X8=40)

ANSWER ANY FIVE QUESTIONS

- 1. a) State Cram's rule and predict the major product formed in the reaction of α phenyl propion aldehyde with methyl magnesium bromide. (2+3)
 - b) Comment on the chirality of the following biphenyls and explain.

(ii)
$$COOH$$
 $COOH$ $COOH$ $COOH$ $COOH$

- 2. a) In what type of solvents the following relative order of reactivity of the halide ion as a nucleophile will be observed and why i) $F^- > Cl^- > B_2^- > I^$
 - ii) $I^- > B_2^- > Cl^- > I^-$ (5)
 - b) Explain why during the acetolysis of eso and endo nor bornyl brosylates, the solvolysis of exo isomer is 350 times faster than the endo isomer. (3)
- 3. a) Give the synthesis of Papaverine. (6)
 - b) Why vinylic and axylhaudes are unreactive towards nucleophilic substitution reaction. (2)
- 4. a) Why neo menthyl chloride undergoes rapid E_2 elimination while in menthyl chloride this elimination is much slower. (5)
 - b) Assign R/S configuration to

$$\begin{array}{c|c} H & SO_3H \\ \hline \\ SO_3H & H \end{array} \tag{3}$$

- 5. What are carbenes? What are the different type of carbenes? Describe the Skell's method to differentiate the types of carbenes. (2+2+4)
- 6. a) E_2 -elimination from meso 2,3 dibromo butane

 NaI in

 acetone

 (5)
 - b) Predict the product and explain

- 7. a) Draw the structures of cis and trans decalins and compare their stability. (5)
 - b) Why chiral amines having a lone pair of electron on the nitrogen atom cannot be resolved. (3)

SECTION – C ANSWER ANY TWO QUESTIONS (20X2=40)

- 8. a) Establish the structure of Zingiberene (15)
 - b) Predict the products A and B. Give the mechanism for the formation of A.

furfural
$$\xrightarrow{alc}$$
 A \xrightarrow{oxidn} B (3+2)

- 9. a) Why α bromo propionate ion on treatment with methanol does not undergo the normal S_N 2 reaction. (5)
 - b) What is E_{ICB} mechanism? What are the requirements for the substrate to undergo E_{ICB} mechanism. (5)
 - c) Explain three factors influencing substitution/elimination ratio. (6)
 - d) In the reaction of S-2- butanol with thionyl chloride to give the corresponding chloride, the reaction proceeds with retention of configuration. Explain. (4)
- 10. a) Give the mechanism for aromatic necrophilic substitution reaction proceeding by elimination-addition type. Mention two evidences in favour of the mechanism. (3+4)
 - b) Give the BAc_2 mechanism for hydrolysis of esters. Mention two evidences in favour of the mechanism. (4+3)
 - c) Explain diastereotopic hydrogens with an appropriate example. (4)
 - d) Which one of the following is a meso compound and why?
 - i) Cis 1,3 dimethyl cyclohexane
 - ii) Cis 1,4 dimethyl cyclohexane (2)