STELLA MARIS COLLEGE (AUTONOMOUS) CHENNAI - 600086
(For candidates admitted during the academic year 2008-08)
SUBJECT CODE : CH/PC/OC14

## M.Sc. DEGREE EXAMINATION, NOVEMBER 2008 <br> BRANCH IV - CHEMISTRY <br> FIRST SEMESTER

REG NO.

| COURSE | $:$ MAJOR - CORE |
| :--- | :--- |
| PAPER | $:$ ORGANIC CHEMISTRY |
| TIME | $: 30$ MINUTES |

## SECTION - A

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

## ANSWER ALL THE QUESTIONS:

I Choose the correct answer:

1. $\mathrm{C}_{\mathrm{H}}^{\mathrm{Br}} \mathrm{C}=\mathrm{C}=\mathrm{C} \underbrace{,^{\prime \prime \mathrm{H}} \text { this allene is }}_{\mathrm{H}}$
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
4. Pyrolysis of amine oxide proceeds by the mechanism
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) $\pm$
6. Boat conformation of cyclohexane has
a) four pairs of eclipsed bond
b) three pairs of eclipsed bond
c) two 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) pyramidal
b) planar
c) square pyramidal
d) trigonal bipyramidal
9. 


a) meso
b) disymmetric
c) achiral
d) Asymmetric
10. Trans-Cyclooctene is chiral due to the presence of
a) Chiral Centre
b) Chiral axis
c) Chiral plane
d) helical structure

## II Fill in the blanks :

11. The configuration of the alkene formed by the elimination of one molar equivalent of HBr from

$\qquad$
$\mathrm{CH}_{3}$
12. The migratory aptitude of aryl group is $\qquad$ than alkyl group.
13. Achiral molecule with one or two proper axis is called $\qquad$ molecule.
14. When in a reaction no bonds to the stereocentre are broken, the reaction proceeds with $\qquad$ in configuration.
15. Cis and trans 1,4-disubstituted cyclehexane are $\qquad$
[chiral/achiral]

## 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.

$$
\mathrm{HC}=\mathrm{C}-\mathrm{C} \equiv \mathrm{C}-\mathrm{CH}=\mathrm{C}=\mathrm{CH}-\mathrm{CH}=\mathrm{CH}-\mathrm{CH}=\mathrm{CH}-\mathrm{CH}_{2} \mathrm{COOH}
$$

17. 


[i]

[ii]

Why [i] is unreactive toward $\mathrm{S}_{\mathrm{N}} 1$ and $\mathrm{S}_{\mathrm{N}} 2$ 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 | $: 21 / 2$ 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 $\alpha$ - phenyl propion aldehyde with methyl magnesium bromide. (2+3)
b) Comment on the chirality of the following biphenyls and explain.
(i)

(ii)

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) $\mathrm{F}^{-}>\mathrm{Cl}^{-}>\mathrm{B}_{2}^{-}>\mathrm{I}^{-}$
ii) $\mathrm{I}^{-}>\mathrm{B}_{2}^{-}>\mathrm{Cl}^{-}>\mathrm{I}^{-}$
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. a) Give the synthesis of Papaverine.
b) Why vinylic and axylhaudes are unreactive towards nucleophilic substitution reaction.
4. a) Why neo menthyl chloride undergoes rapid $E_{2}$ elimination while in menthyl chloride this elimination is much slower.
b) Assign R/S configuration to

ii)

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

b) Predict the product and explain

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

## SECTION - C <br> ANSWER ANY TWO QUESTIONS

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

$$
\begin{equation*}
\text { furfural } \xrightarrow[\mathrm{KCN}]{\text { alc }} \mathrm{A} \xrightarrow{\text { oxidn }} \mathrm{B} \tag{15}
\end{equation*}
$$

9. a) Why $\alpha$-bromo propionate ion on treatment with methanol does not undergo the normal $\mathrm{S}_{\mathrm{N}} 2$ reaction.
b) What is $\mathrm{E}_{\text {ICB }}$ mechanism? What are the requirements for the substrate to undergo $\mathrm{E}_{\text {ICB }}$ mechanism.
c) Explain three factors influencing substitution/elimination ratio.
d) In the reaction of S-2-butanol with thionyl chloride to give the corresponding chloride, the reaction proceeds with retention of configuration. Explain.
10. a) Give the mechanism for aromatic necrophilic substitution reaction proceeding by elimination-addition type. Mention two evidences in favour of the mechanism.
b) Give the $\mathrm{BAc}_{2}$ mechanism for hydrolysis of esters. Mention two evidences in favour of the mechanism.
c) Explain diastereotopic hydrogens with an appropriate example.
d) Which one of the following is a meso compound and why?

$$
\begin{align*}
& \text { i) } \begin{array}{l}
\text { Cis - 1,3-dimethyl cyclohexane } \\
\text { ii) } \\
\text { Cis - 1,4-dimethyl cyclohexane }
\end{array}
\end{align*}
$$

