# M.Sc. DEGREE EXAMINATION, NOVEMBER 2010 <br> BRANCH IV - CHEMISTRY <br> FIRST SEMESTER 

REG NO. $\qquad$

| COURSE | $:$ MAJOR - CORE |
| :--- | :--- |
| PAPER | $:$ ORGANIC CHEMISTRY - I |
| 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. Which one of the following is a non classical carbocation
a. $\mathrm{CH}_{3}-\stackrel{+}{\mathrm{C}} \mathrm{H}-\mathrm{CH}_{3}$
b.

c. $\mathrm{CH}_{2}=\stackrel{+}{\mathrm{C}} H$
d. $\mathrm{CH}_{3}-\stackrel{+}{\mathrm{C}}-\mathrm{CH}_{3}$
$\mathrm{CH}_{3}$
2. In the conversion of chlorobenzene to aniline using $\mathrm{NaNH}_{2} /$ liq $\mathrm{NH}_{3}$ the intermediate formed is
a. Carbanion
b. Carbocation
c. Benzyne
d. Free radical
3. The reagent used to transform

a. $\mathrm{Na} / \mathrm{liq} \mathrm{NH}_{3}$
b. $\mathrm{LiAlH}_{4}$
c. $\mathrm{NaBH}_{4}$
d. $\mathrm{H}_{2}$ / Raney nickel
4. For an electron withdrawing substituent the $\sigma$ value is
a. positive
b. negative
c. zero
d. none of the above
5. If the introduction of a polar substituent has no effect upon the equilibrium constant then $\rho$ value is
a. positive
b. negative
c. zero
d. sometimes +ve or -ve depending on the reaction.
6. Which among the following is a bridgehead carbocation
a. $\mathrm{C}_{6} \mathrm{H}_{5}-\mathrm{CH}_{2}$
b. $\mathrm{CH}_{2}=\mathrm{CH}-\mathrm{CH}_{2}$
c.

d.

7. The necessary and sufficient condition for a molecule to be optically active is it should have
a. Chiral centre
b. Chiral plane
c. Chiral axis
d. chirality
8. Geometrical isomers are
a. enantiomers
b. diastereoisomers
c. position isomers
d. functional isomers
9. Trans 1,2 dibromocyclohexane is
a. Chiral
b. achiral
c. meso
d. racemic
10. Which of the following carbocation is more stable
a.

b.

c.

d.


## II Fill in the blanks:

11. An example for a $\pi$ deficient non - benzenoid aromatic hydrocarbon is $\qquad$
12. The Fischer projection of a molecule corresponds to ----------- conformation of the molecule.
13. According to Hammond postulate in $\qquad$ reaction the structure of the transition state is energetically closer to the reactant.
14. In Diels -Alder reaction Benzyne is a powerful $\qquad$
15. The stereochemical outcome of a reaction proceeding by neighbouring group participation is $\qquad$ in configuration .

## III Answer the following in one or two sentences:

16. In the preparation of picric acid from phenol it is first sulphonated and then nitrated. Why?
17. Differentiate asymmetry from dissymmetry.
18. Draw the structure of a stable free radical used as standard in ESR spectroscopy.
19. Draw the structure of a molecule which is optically active due to the presence of a chiral plane.
20. $R-{ }_{\|}^{C}-\left.\right|_{N} ^{R}-B r$ does not undergo Hoffmann rearrangement. Why?

## $A A A A A A A A A A A$

STELLA MARIS COLLEGE (AUTONOMOUS) CHENNAI - 600086
(For candidates admitted during the academic year 2009-2010 \& thereafter)
SUBJECT CODE : CH/PC/OC14

## M.Sc. DEGREE EXAMINATION, NOVEMBER 2010 <br> BRANCH IV - CHEMISTRY <br> FIRST SEMESTER

COURSE : MAJOR - CORE
PAPER : ORGANIC CHEMISTRY - I
TIME : $\mathbf{2}^{1 ⁄ 2}$ HOURS
MAX. MARKS : 80
SECTION - B
$(5 \times 8=40)$

## ANSWER ANY FIVE QUESTIONS

1. Explain by taking a suitable example how kinetic studies and labeling method help in the elucidation of reaction mechanism .
2. a) Predict the order of stability of the following carbanions and explain.

$$
\begin{equation*}
R_{2} C=C H^{-}, \quad R_{3} C-C H_{2}, \quad R-C \equiv C^{\ominus} \tag{3}
\end{equation*}
$$

b) Compare the rate of acetolysis of the following norbornane derivatives and explain.

I

II
3. Account for the following
a) Compound I loses its proton in hydrogen exchange reaction 6000 times slowly than compound II. Why?


I


II
b) Cyclooctatetraene is a tub shaped molecule. Why?
c) Azulene an aromatic hydrocarbon has a dipole moment value of 0.8 debye units.
4. Explain Sharpless asymmetric epoxidation . Give its mechanism .
5. Addition of bromine to maleic and fumaric acid is stereospecific and stereoselective Explain.
6. Give the mechanism for the following reactions
a. Woodward and Prevost hydroxylation
b. Robinson annulation
$(4+4)$
7. Predict the product in the following rearrangement reactions and give the mechanism $(3+3+2)$
a)

b)

c)


## SECTION - C

## ANSWER ANY TWO QUESTIONS

(20X2=40)
8. a) What is Hammett equation ? Explain the terms involved in it .Why is it called a linear free energy relationship ?
$(2+2+3)$
b) What are carbenes? What are the different types of carbenes? Explain the Skell's method to differentiate the types of carbenes .
$(2+2+4)$
c) Classify the following compounds as aromatic, antiaromatic non-aromatic and homoaromatic
(i)

(iv)

(ii)

(iii)

(v)

9. a) Predict the product in the following aromatic electrophilic substitution reaction.
(i)

(ii)

(iii)

b) Account for the fact that aryl group has - I effect but it is activating and $\mathrm{o}, \mathrm{p}$ orienting.
c) How will you prepare the compound given below? Give the mechanism of the reaction.

d) How the configuration of unsymmetrical ketoximes is established by Beckman rearrangement.
e) Draw the structure of the diene and the dienophile which upon reaction will give each of the following product.
(i)

(ii)

10. a) Designate the hydrogens in the following molecule as enantiotopic, diastreotopic and Homotopic .
(i)

(ii)

(iv)

b) Comment on the stereoisomerism of 1,3 dimethyl cyclohexane .
c) A suitably substituted adamantane has four chiral centers, yet it exists only as a pair of enantiomers. Why?

d) Assign R / S and E / Z notation to the following compounds
(i)
(ii)

(iii)
(iv)


(v)

(vi)


