## STELLA MARIS COLLEGE (AUTONOMOUS) CHENNAI - 600 086

(For candidates admitted during the academic year 2009 – 2010 & thereafter)

**SUBJECT CODE: CH/PC/OC14** 

### M.Sc. DEGREE EXAMINATION, NOVEMBER 2010 **BRANCH IV - CHEMISTRY** FIRST SEMESTER

**REG NO.**\_\_\_\_\_

COURSE : MAJOR - CORE

: ORGANIC CHEMISTRY - I **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. Which one of the following is a non classical carbocation

a. 
$$CH_3 - \overset{+}{C}H - CH_3$$

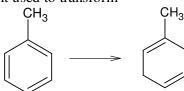
b. 
$$\nearrow$$
  $CH_2$ 

c. 
$$CH_2 = \overset{+}{C}H$$

a. 
$$CH_3 - \overset{+}{C}H - CH_3$$
 b.  $CH_2 = \overset{+}{C}H$  d.  $CH_3 - \overset{+}{C} - CH_3$ 

- 2. In the conversion of chlorobenzene to aniline using NaNH 2/ liq NH3 the intermediate formed is
  - a. Carbanion
- b. Carbocation
- c. Benzyne
- d. Free radical

3. The reagent used to transform



- a. Na / liq NH<sub>3</sub>
- b. LiAlH<sub>4</sub>
- c. NaBH<sub>4</sub>
- d. H<sub>2</sub> / 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

$$a. C_6H_5 - CH_2$$

a. 
$$C_6H_5 - \overset{\bigoplus}{C}H_2$$
 b.  $CH_2 = CH - \overset{\bigoplus}{C}H_2$  c.  $\overset{\bigoplus}{\triangleright}CH_2$  d.

c. 
$$\hookrightarrow$$
  $CH_2$ 



- 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

$$a. \quad \text{NC} \longrightarrow \hspace{-0.5cm} \bigoplus_{\text{CH}_2} \hspace{-0.5cm} \bigoplus_{\text{CH}_2} \hspace{-0.5cm}$$

b. 
$$CI \longrightarrow CH_2$$

$$d.$$
  $O_2N$ — $CH_2$ 

#### II Fill in the blanks:

- 11. An example for a  $\pi$  deficient non benzenoid aromatic hydrocarbon is -----
- 12. The Fischer projection of a molecule corresponds to ----- conformation of the molecule.
- 13. According to Hammond postulate in ----- reaction the structure of the transition state is energetically closer to the reactant.
- 14. In Diels –Alder reaction Benzyne is a powerful -----.
- 15. The stereochemical outcome of a reaction proceeding by neighbouring group participation is ------ 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.
- R|
  20. R C N Br does not undergo Hoffmann rearrangement . Why?

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**COURSE : MAJOR - CORE** 

PAPER : ORGANIC CHEMISTRY - I

TIME : 2½ HOURS MAX. MARKS : 80

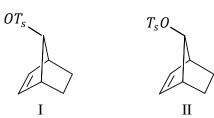
SECTION - B (5X8=40)

#### **ANSWER ANY FIVE QUESTIONS**

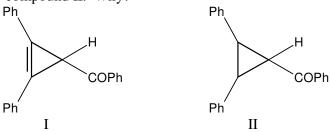
- 1. Explain by taking a suitable example how kinetic studies and labeling method help in the elucidation of reaction mechanism.
- 2. a) Predict the order of stability of the following carbanions and explain. (3)

$$R_2C=CH^-$$
 ,  $R_3C-CH_2$  ,  $R-C\equiv C^{\scriptsize \scriptsize \bigcirc}$ 

b) Compare the rate of acetolysis of the following norbornane derivatives and explain. (5)



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

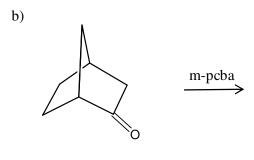


- b) Cyclooctatetraene is a tub shaped molecule . Why? (3)
- c) Azulene an aromatic hydrocarbon has a dipole moment value of 0.8 debye units. {2}
- 4. Explain Sharpless asymmetric epoxidation. Give its mechanism.
- 5. Addition of bromine to maleic and fumaric acid is stereospecific and stereoselective 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) OH OH
$$C_{6}H_{5}-\overset{|}{C}-\overset{|}{C}-\overset{|}{C}-CH_{3} \longrightarrow HT \longrightarrow$$



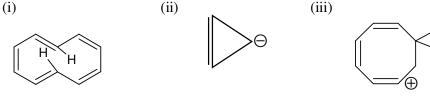
c) 
$$\xrightarrow{O}$$
  $\xrightarrow{OH}$ 

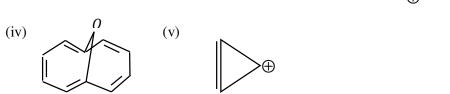
**SECTION - C** 

### 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 (5)





..3

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

(i)  $\begin{array}{c} CI \\ \hline \\ HNO_3 / H_2SO_4 \\ \hline \end{array}$ 

COOH

(ii)  $\begin{array}{c} \text{OH} \\ \text{CH}_3 \\ \hline \end{array} \xrightarrow{\text{Br}_2/\,\text{FeBr}_3} \rightarrow$ 

(iii) CI  $CI_2/AICI_3$ 

- b) Account for the fact that aryl group has I effect but it is activating and o , 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. (5)

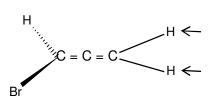
 $(i) \qquad \qquad H \qquad O \qquad \qquad (ii) \qquad \qquad COOH$ 

..4

(3)

10. a) Designate the hydrogens in the following molecule as enantiotopic, diastreotopic and Homotopic . (4)

(i)



(iii)



- b) Comment on the stereoisomerism of 1, 3 dimethyl cyclohexane. (5)
- 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
- (6 + 2)

(i)

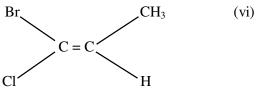
$$\begin{array}{c} \mathsf{COOH} \\ | \\ \mathsf{C}_{\text{\tiny $N$}} \\ \mathsf{H}_2 \mathsf{N} & \mathsf{CH}_3 \end{array}$$

(ii)

(iii)

(iv)

(v)



$$O_2N$$
  $C = C$   $CH_2CH_3$   $CH_3$