STELLA MARIS COLLEGE (AUTONOMOUS) CHENNAI-86
(For candidates admitted during the academic year 2011-12)

SUBJECT CODE: 11CH/PC/OM14

M.Sc. DEGREE EXAMINATION, NOVEMBER 2011
BRANCH IV- CHEMISTRY
FIRST SEMESTER

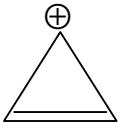
REG.NO ……..

COURSE: CORE
PAPER : ORGANIC REACTION MECHANISMS AND STEREOCHEMISTRY
TIME : 30 MINUTES **MAX.MARKS : 20**

SECTION – A (20x1=20)
ANSWER ON THE QUESTION PAPER ITSELF.
Answer all the questions.

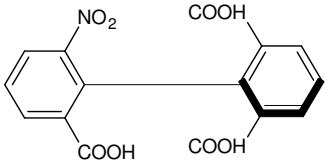
I Choose the correct answer:

1. In acetaldehyde the two faces of the double bond are
   a) enantiotopic b) diastereotopic c) stereotopic d) homotopic

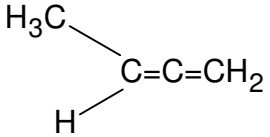
2.  is an
   a) Aromatic compound b) Benzenoid aromatic compound
   c) non- benzenoid aromatic compound d) Antiaromatic compound

3. Prevost method of hydroxylation gives
   a) Cis diol b) trans diol c) Both cis and trans diol d) Cis – diacetate

4. Sharpless asymmetric epoxidation involves the use of
   a) chiral solvent b) chiral catalyst c) chiral reagent d) chiral substrate

5.  is
   a) chiral b) achiral c) racemic d) resolvable

II Fill in the blanks:

6. The rearrangement used to determine the configuration of ketoximes is ----------.
7. The reagent used to oxidize a methylene group to carbonyl group is ----------.
8. The stereochemical outcome of a reaction proceeding by neighbouring group participation is ---------- in configuration.
9.  is optically ----------.
10. Trans decalin has ---------- conformation.

..2

III State whether the following statements are True or False:

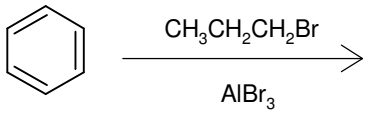
11. Azulene is a colourless molecule.
12. Cummulenes having odd number of double bonds exhibit enantiomerism.
13. Cis- 1,3 – cyclohexane diol has a plane of symmetry.
14. Acyloin condensation involves the formation of carbonium ion as intermediate,
15. An erythro isomer has similar groups at two adjacent chiral centers on the same side of the Fischer projection.

iV Answer in one or two sentences:

16. State Hammond postulate.

17. Is trans cyclooctene chiral, if yes explain.

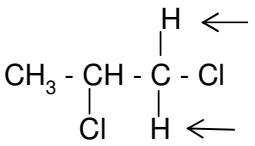
18. Predict the product and write the mechanism.



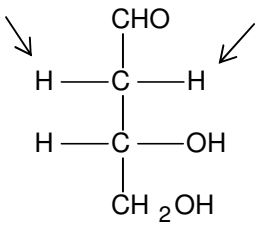
19. How do the terms asymmetric and dissymmetric differ?

20. Designate the hydrogens shown by arrows in the following compounds as enantiotopic or diastereotopic

a)



b)



****

STELLA MARIS COLLEGE (AUTONOMOUS) CHENNAI-86
(For candidates admitted during the academic year 2011-12)

SUBJECT CODE: 11CH/PC/OM14

M.Sc. DEGREE EXAMINATION, NOVEMBER 2011
BRANCH IV- CHEMISTRY
FIRST SEMESTER

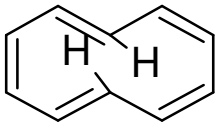
COURSE: CORE
PAPER : ORGANIC REACTION MECHANISMS AND STEREOCHEMISTRY
TIME : 2½ HOURS **MAX.MARKS : 80**

SECTION – B **(5x8=40)**

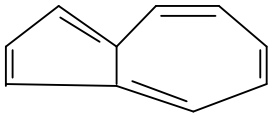
Answer any five questions:

1. How identification of the products and isotopic labeling studies help in the elucidation of reaction mechanism ? [4 + 4]
2. a) Predict whether the following compounds are aromatic / non- aromatic/ antiaromatic and homoaromatic . [6 x1 = 6]

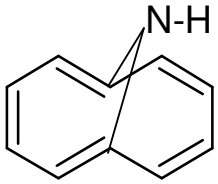
(i)



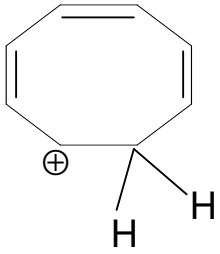
(ii)



(iii)



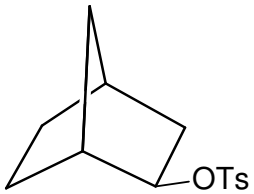
(iv)



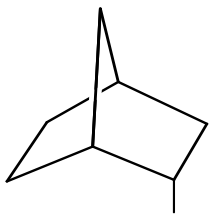
(v)

(vi)

b) Why acetolysis of compound A takes place 350 times faster than that of compound B? [2]



A

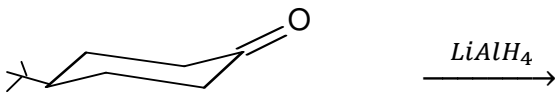


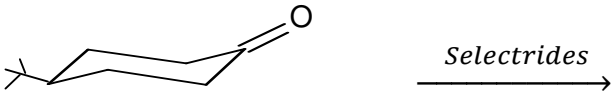
B

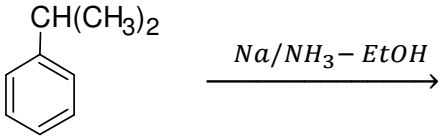
..2

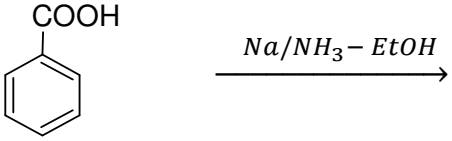
3. Predict whether the following compounds are optically active or not .Explain your answer [4 x2 = 8]
   a) trans – 1,2 – dimethyl cyclopropane
   b) cis - 1,2 – dimethyl cyclobutane
   c) trans - 1,2 – dimethyl cyclobutane
   d) trans - 1,2 – dimethyl cyclopentane

4. Predict the product and explain [4 x 2 = 8]

a) 

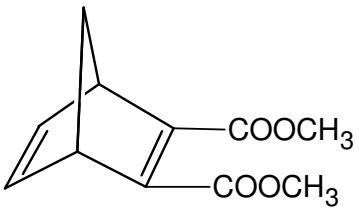
b) 

c) 

d) 

5. What are singlet and triplet carbenes ? Discuss their geometry. Name the rearrangement where carbenes are formed as intermediates and give the mechanism [4 + 2+ 2 = 8]

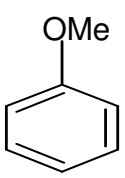
6. a) What is Hammett equation ? Explain the terms in it .What are the limitations of Hammett equation? [4]
   b) Which diene and dienophile would you employ to synthesize the compound? [4]

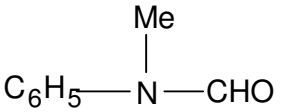


7. Predict the product of the following reaction and name the reaction

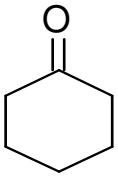
a) Acetophenone $\xrightarrow{CF_3COOH}$ [2]

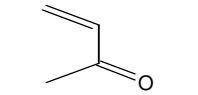
b) RCOOAg + Br_2 $\longrightarrow$ [1]

c) 



[2]

d) 



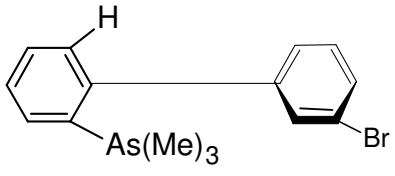
A $\xrightarrow[2)\ dehydration]{1)\ aldol\ condnsation}$ B [3]

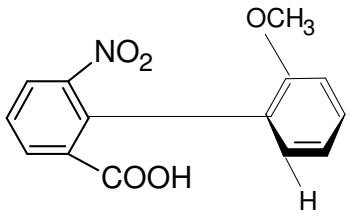
SECTION – C

Answer any two questions. **(2x20=40)**

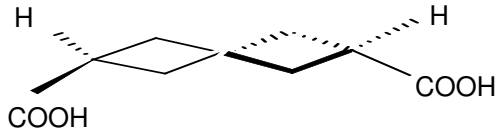
8. a) Give evidence for the formation of cyclopropanone intermediate (via) an intramolecular 1,3- elimination involving a back side attack of the carbanion in Favorskii rearrangement. [5]
   b) What are homoaromatic compounds? Explain with an example. [5]
   c) Comment on the chirality of 2,3 – pentadiene [5]
   d) What is Cope elimination? Give the mechanism of the reaction [5]

9. a) Give the mechanism of the following reactions
      i) Stork Enamine reaction
      ii) Stobbe condensation [4 x 2 = 8]
   b) Assign R/S configuration to the following compounds [6 x 2 = 12]

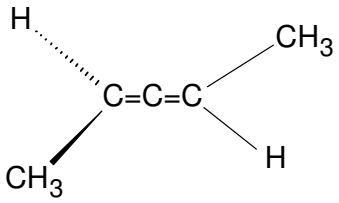
i) 

ii) 

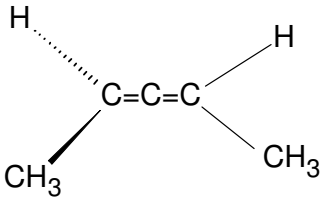
iii)



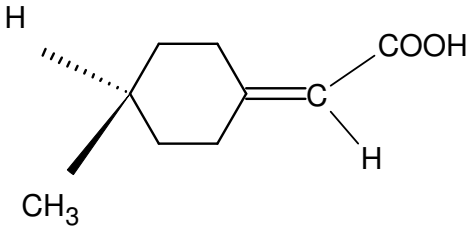
iv)



v)



vi)

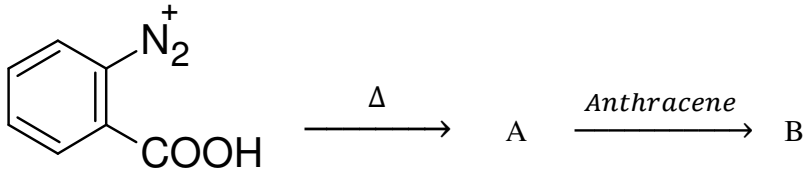


10. a) Describe the NMR spectrum of a diatropic and paratropic compound by taking an example. [6]

b) Using Cram's rule, predict the major product from the reaction of phenylpropionaldehyde with methylmagnesium bromide [5]

c) Draw the Fischer projection ,staggered Newmann and Sawhorse structure for threo- 2,3- dichloro-3-phenylpropanoic acid [6]

d) Predict the product [3]



****