

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

SUBJECT CODE: 11CH/PC/OM14

M.Sc. DEGREE EXAMINATION, NOVEMBER 2014
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:

- The molecules which have stereo heterotropic ligands as in propionic acid are called
 - Chiral molecule
 - Achiral molecule
 - Prochiral molecule
 - Symmetric molecule
- In Wagner Meerwein rearrangement the intermediate formed is a
 - Carbocation
 - Carbanion
 - Carbon free radical
 - Aryne
- The conversion of the tosyl hydrazone of an aldehyde or a ketone to a less substituted alkene by using a strong base is called
 - Peterson Synthesis
 - Shapiro reaction
 - Cope elimination
 - Hoffmann elimination
- cis- 9-methyl Decalin has
 - 2 Butane Gauche interactions
 - 3 Butane Gauche interactions
 - 4 Butane Gauche interactions
 - 5 Butane Gauche interactions
- Triptycene is formed by trapping of
 - Carbene
 - Nitrene
 - Benzyne
 - Radicals

II Fill in the blanks:

- Diatropic compounds are otherwise called _____ compounds.
- trans 1,2 dichlorocyclopropane is optically _____.
- The reactive intermediate in Wittig rearrangement is _____.
- The dienes in Diels Alder reaction should have _____ conformation.
- Cross over experiments are carried out to find whether the rearrangement is _____ or _____.

III State whether True or False:

11. The structure - activity relationship applicable to aliphatic compounds is Hamett equation
12. The Woodward method of hydroxylation results in trans – diol.
13. In Beckmann rearrangement the group that migrates towards electron deficient nitrogen atom is cis to the leaving group.
14. In acyloin condensation free radicals are formed as intermediates.
15. The two faces of the double bond in cis- but-2-ene are enantiotopic.

IV Answer in one or two sentences:

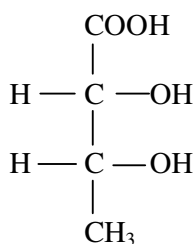
16. What are pseudo aromatic compounds? Give an example.

17. What are enamines ?What are its uses?

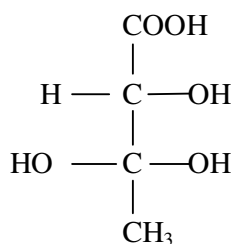
18. What are σ^+ and σ^- constants in Hammett equation ?

19. What are non- classical carbocations?

20. Classify the following compounds as Erythro / Threo.



I



II

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TIME : 2½ HOURS

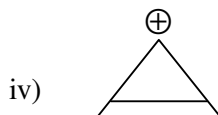
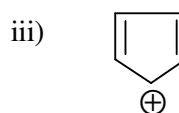
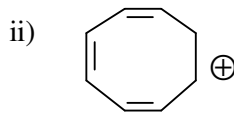
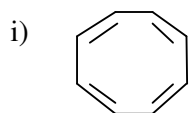
MAX.MARKS : 80

SECTION – B

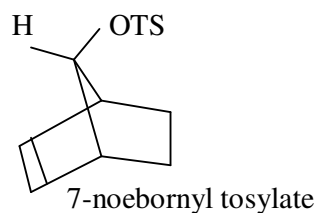
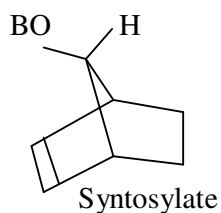
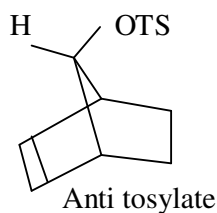
(5x8=40)

Answer any five questions:

- How isotopic labelling and trapping of an intermediate help in elucidating reaction mechanism. [5]
 - What is formylation reaction? What are the different methods to formylate the benzene ring? [3]
- Give the mechanism for Wolff rearrangement? How does thermal Wolff rearrangement differ from photochemical Wolff rearrangement? [8]
- Predict whether the following compounds are aromatic, antiaromatic, non – aromatic and homoaromatic? [5]



- Azulene an isomer of naphthalene is a blue coloured solid with a dipole moment of 0.8 debye units. Why? [8]
- The relative rates of solvolysis of syn, anti-7-norbornenyl tosylate and 7-norbornyl tosylate are given below. 7-norbornyl tosylate = 1, anti-7-norbornenyl tosylate = 10^{11} , syn-7-norbornenyl tosylate = 10^7 . Account for the results. [5]



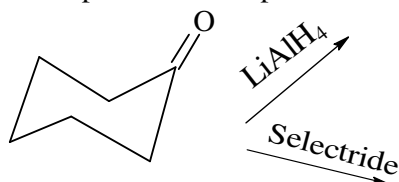
- How will effect the following transformation via Birch reduction. [3]



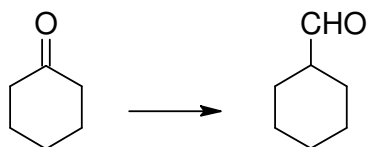
5. a) Using Cram's rule predict the major product from the reaction of α -phenyl Propionaldehyde with MeMgBr. [5]

b) How many stereoisomers are possible for 1,2-dichlorocyclopentane. Discuss their activity. [3]

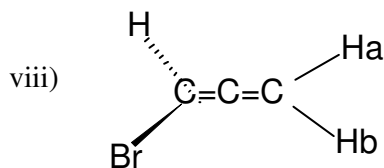
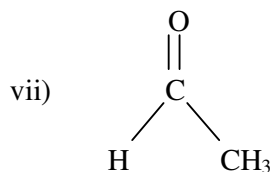
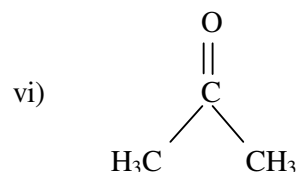
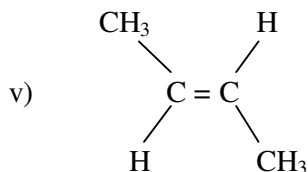
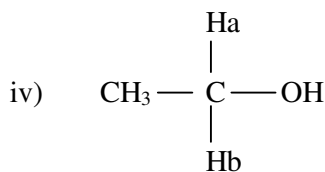
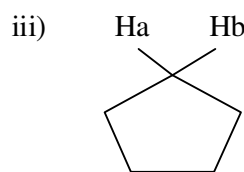
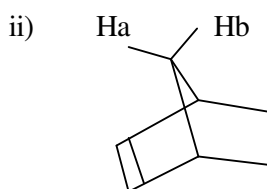
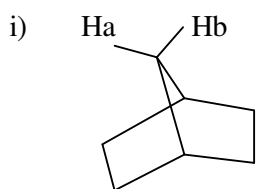
6. a) Predict the product and explain. [5]



b) How will you convert via Wittig reaction? [3]



7. Identify the hydrogens / faces of the double bond in the following compounds as homotopic, enantiotopic and diastereotopic. [8]

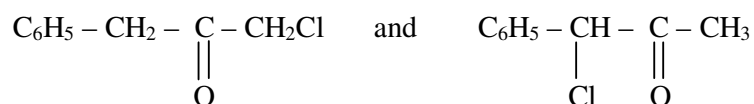


SECTION – C

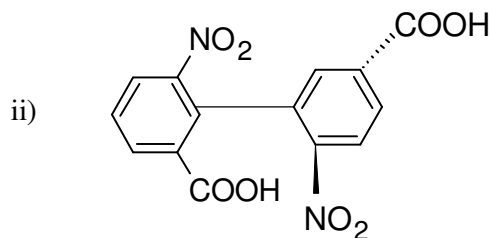
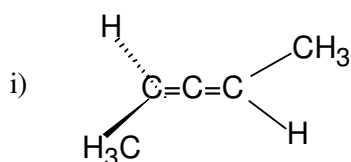
Answer any Two questions.

(2x20=40)

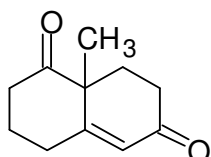
8. a. What are stereospecific and stereoselective reactions? Explain each with an example. [7]
- b. What is Hammett equation? Explain the terms involved in it . What are the limitations of Hamett equation? [6]
- c. Why the isomeric haloketones I and II give the same product on Favourskii reaction when treated with aqueous base. [4]



- d. Assign R & S configuration to the following compounds. [3]



9. a. What is Robinson Annulation reaction? How will you prepare the compound given below. [6]



- b. Give the Baldwin's rule for ring closure reaction . [5]
- c. What is endo rule as applied to Diel's Alder reaction. [3]
- d. Give the preferred conformation for the following compounds and explain. [6]
- cis- Cyclohexane 1,3- diol
 - cis – 1,4 ditertiary butyl cyclohexane
 - trans 1,2 – dibromocyclohexane

10. a. Write the Fischer projection for (2S,3R) -3-bromo-2-butanol . Convert this to Sawhorse and Perspective drawing. [8]

b. Give the mechanism for [8]

i) Hunsdiecker reaction

ii) Mannich reaction

c. Predict the Product [4]

