

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 2012
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:

- Allylic oxidation of olefins is
a) stereoselective b) stereospecific c) regiospecific d) regioselective
- The type of process that can successfully be treated by Marcus theory is
a) E1 b) S_N1 c) S_N2 d) none of the above
- Curtius rearrangement involves _____ intermediate.
a) carbene b) aryne c) carbanion d) nitrene
- Cyclopentadienyl anion is
a) aromatic b) antiaromatic c) homoaromatic d) non aromatic
- Erythro-2R,3S-butanediol is
a) optically active b) optically inactive c) diastereoisomer d) cannot predict

II Fill in the blanks:

- Baldwin rules are applied to _____ compounds.
- Opposite to Oppenauer oxidation is _____ reduction.
- The carbanion in the Wittig reaction is called as _____.
- An example for pseudoaromatic compound is _____.
- trans-1,2-dihydroxycyclohexane is optically _____.

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TIME : 2½ HOURS

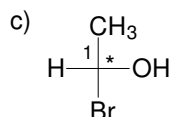
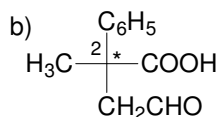
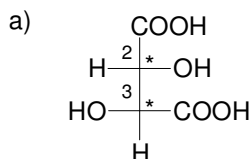
MAX.MARKS : 80

SECTION – B

(5x8=40)

Answer any five questions:

1. Explain Linear Free Energy Relationship in Hammett equation. How is it explained in Taft equation? (4+4)
2. How cross over experiments can prove inter or intramolecular rearrangement reactions? Give reasons with examples. (4+4)
3. Compare Wolff Kishner and Clemmensen reduction reactions with suitable examples. (4+4)
4. a) Illustrate the effect of isotope to explain the mechanism of Favorskii rearrangement reaction. (4)
b) How is the formation of aryne intermediate confirmed during the aryne dimerization reaction? (4)
5. a) Is cyclohexatriene aromatic or antiaromatic? Explain with suitable evidences. (3)
b) Identify the following compounds as aromatic, non-aromatic, antiaromatic, homoaromatic or pseudoaromatic. (5)
i) 1,3,5-cyclohexatriene ii) [14]-annulene iii) 1,3,5-heptatrienyl cation
iv) 1,3-cyclopentadiene v) azulene
6. Draw Fischer, Sawhorse and Newmann projections of 2R,3R-dibromopentane. (2+3+3)
7. Assign R or S configurations to the following compounds at the starred carbon atoms. (8)



SECTION – C

Answer any two questions.

(2x20=40)

8. a) How does Hammond Postulate determine the shape of intermediate in a chemical reaction? (4)
b) Discuss in detail the kinetic methods of determining the mechanism of a reaction? (8)
c) Discuss Stobbe condensation reaction. (4)
d) Explain the mechanism of Birch reduction. (4)
9. a) Compare SeO_2 oxidation in 2-phenylacetone and toluene. (3+3)
b) Write short notes on aqueous and nonaqueous Cr(VI) oxidation reactions. (3+3)
c) Compare the reactivity of CH_3 , H and phenyl groups in neighbouring group participation of pinacol pinacolone rearrangement. (8)
10. a) Define i) prochirality ii) enantiotopic hydrogens. (2+2)
b) Compare the reactivity of cis and trans isomers in 1,2-disubstituted cyclohexanes towards hydrolysis reaction. (8)
c) Elucidate Sharpless asymmetric epoxidation reaction. (6)
d) Name the following compound. (2)

