

STELLA MARIS COLLEGE (AUTONOMOUS) CHENNAI-86
(For candidates admitted during the academic year 2015-16)

SUBJECT CODE: 15CH/PC/OC14

M.Sc. DEGREE EXAMINATION, NOVEMBER 2015
BRANCH IV- CHEMISTRY
FIRST SEMESTER

REG.NO

COURSE: CORE

PAPER : ORGANIC CHEMISTRY - I

TIME : 30 MINUTES

MAX.MARKS : 20

SECTION – A

(20x1=20)

ANSWER ON THE QUESTION PAPER ITSELF

Answer all the questions.

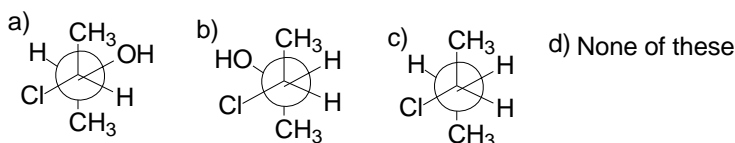
I Choose the correct answer:

1. IUPAC name for the following compound is

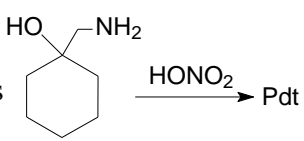


- a) spiro[4,5]dodeca-1,6-diene
b) spiro[5,4]dodeca-1,6-diene
c) spiro[4,5]dodeca-1,6-diene
d) bicyclo[5.4.1]decane

2. The enantiomer of threo-3-chlorobutan-2-ol is



3. Which of the following compound is not aromatic?
a) cyclopentadienyl anion
b) tropylium cation
c) cyclopentadienyl cation
d) pyridine
4. 1,3,5-cycloheptatriene can be converted to an aromatic compound by
a) H⁺ abstraction
b) H⁻ abstraction
c) H atom abstraction
d) H₂ elimination
5. In the boat conformation of cyclohexane, the most destabilizing interaction is
a) eclipsing
b) 1,3-diaxial
c) 1,3-diequatorial
d) flagpole-flagpole
6. Which of the following agents form *trans*-2-butene with 2-butyne?
a) H₂/Pt
b) Zn/HCl
c) Na/Liq.NH₃
d) Lindlar' catalyst
7. Enantiomorphs cannot be separated by
a) fractional crystallization
b) fractional distillation
c) use of enzymes
d) chromatography by alumina
8. Solvolysis reaction of diastereomeric *exo*- and *endo*-2-norbornyl tosylate in acetic acid gives
a) *exo*-2-norbornyl acetate
b) *endo*-2-norbornyl acetate
c) both a & b
d) none of the above

9. The end product of the above reaction is . The starting material is cyclohexane-1,2-diol, a six-membered ring with hydroxyl groups at the 1 and 2 positions. The reaction arrow is labeled with HONO₂ above and Pd below. The options are: a) cyclohexanone, b) cycloheptanone, c) cyclopentanone, d) cyclohexanol.
10. Hammett equation is
 a) $\rho = \sigma \log(k/k_0)$ b) $\log(k/k_0) = \sigma/\rho$ c) $\log(k/k_0) = \sigma\rho$ d) none of the above

II Fill in the blanks:

11. ¹H NMR signal of inner protons of annulene is observed in _____ region.
12. Cyclooctatetraene is _____ (aromatic/anti/nonaromatic).
13. *trans*-1,3-dimethylcyclobutane is optically _____ (active/inactive).
14. In CH₃CH₂OH molecule, the shaded hydrogen is called _____.
15. An alkene A on Cl₂ addition reaction forms 2R,3S-2,3-dichlorobutane. A is _____.
16. The catalyst used in the Sharpless asymmetric epoxidation reaction is- _____.
17. (C₆H₅)₃CH₂Cl undergoes hydroxylation much faster rate than (CH₃)₃CH₂Cl due to _____.
18. _____ is a short-lived unstable molecule in a reaction which is formed in between the reaction when reactants change into products.
19. Neopentyl chloride on hydroxylation forms _____.
20. Hammett equation fails with aliphatic compounds due to _____.

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TIME : 2½ HOURS

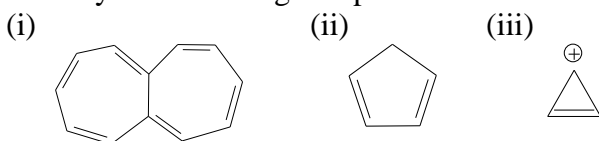
MAX.MARKS : 80

(5x8=40)

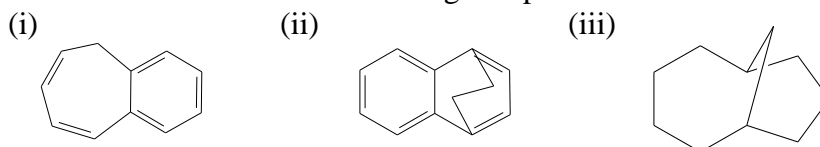
SECTION – B

Answer any five questions:

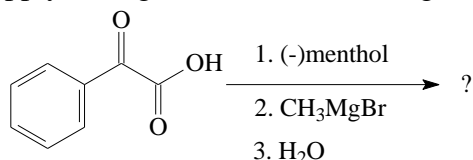
1. Classify the following compounds in to aromatic/antiaromatic/nonaromatic.



2. Give IUPAC name for the following compounds.



3. Discuss the optical isomerism exhibited by allenes and biphenyl derivatives.
4. Explain the use of chiral reagents in asymmetric synthesis using two suitable examples.
5. Discuss the conformation analysis of 1,2-, 1,3- and 1,4-dimethylcyclohexanes.
6. Apply Prelog rule for the following reaction and predict the product.



7. Explain the determination of the mechanism of a chemical reaction by isotopic labeling technique.

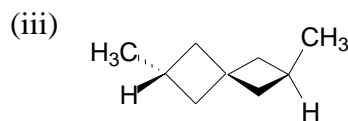
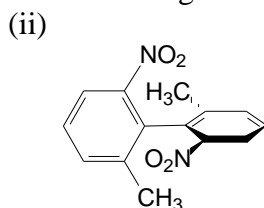
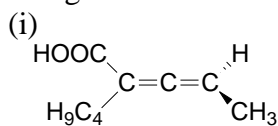
SECTION – C

Answer any Two questions.

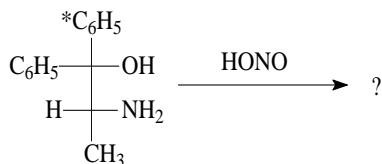
(2x20=40)

8. a. The proton NMR signals of [18]annulene with 6 inner protons are highly shielded (at -3 ppm) whereas dianion of [18]annulene protons are strongly deshielded (at 20.8 ppm and 29.5 ppm). Explain Why? (5)
- b. Explain the use of chiral auxiliaries in the Evan aldol synthesis. (5)
- c. Explain Cram's rule with suitable examples. (6)
- d. *cis*-4-*tert*-butylchlorocyclohexane eliminate HCl much more readily than do the corresponding trans isomers. Explain why? (4)

9. a. Discuss the stereochemistry of the epoxidation reaction of olefins. (5)
- b. Assign R/S notation for the following. (3)



- c. Apply Curtin-Hammett principle and predict the product for the following reaction. (6)



- d. Discuss the stereochemistry of the reactions of *cis*- & *trans*-2-aminocyclohexanol with HONO. (6)

10. a. Explain the crossover experiment and microscopic reversibility methods of determination of mechanism of a chemical reaction. (10)
- b. Calculate the pka value of 2,4,5-trinitrobenzoic acid from the following data. [pka of benzoic acid = 4.2, $\sigma_{p\text{-nitro}} = 0.78$, $\sigma_{m\text{-nitro}} = 0.71$, $\rho_{\text{ionization}} = 2.3$]. (5)
- c. Explain the influence of polar substituent in hydrolysis of ester in acidic and basic catalysts using Hammett relationship. (5)
