

PSG COLLEGE OF ARTS & SCIENCE
(AUTONOMOUS)

MSc DEGREE EXAMINATION DECEMBER 2022
(First Semester)

Branch - CHEMISTRY

ORGANIC REACTION MECHANISM AND STEREOCHEMISTRY

Time: Three Hours

Maximum: 50 Marks

SECTION-A (5 Marks)

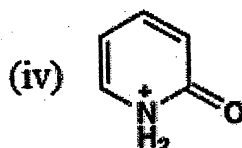
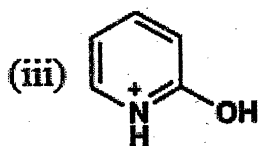
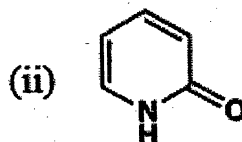
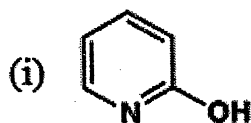
Answer ALL questions

ALL questions carry EQUAL marks

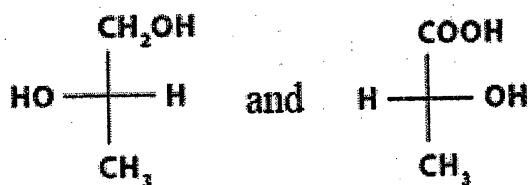
(5 x 1 = 5)

- 1 Which among the following groups exhibit the +I effect?
(i) -Br and -CH₃ (ii) -COOR and -OR
(iii) -CH₂R and C₆H₅O⁻ (iv) -OH and -COOR

- 2 Which among the following is not an aromatic compound?



- 3 In the electrophilic aromatic substitution reactions, the halogens are
(i) *o*-, *p*- directing and deactivating (ii) *m*-directing and activating
(iii) *m*-directing and deactivating (iv) *o*-, *p*- directing and activating
- 4 The rearrangements which involve the transformation of a lesser stable carbonium ion into a more stable carbonium ion is called as
(i) Sommelet-Hauser rearrangement (ii) Curtius rearrangement
(iii) Favorskii rearrangement (iv) Wagner-Meerwin rearrangement
- 5 In the Assignment of R and S for the compounds respectively which is the correct notation?



- (i) R and S (ii) S and R
(iii) R and R (iv) S and S

SECTION - B (15 Marks)

Answer ALL Questions

ALL Questions Carry EQUAL Marks

(5 x 3 = 15)

- 6 a Outline the resonance structures of aniline and nitrobenzene.
OR
b Narrate any three factors which affect the strength of acids and bases.

Cont...

- 7 a Mention the significance of Frost and Musulin diagram. State any two rules for drawing the Frost circles.

OR

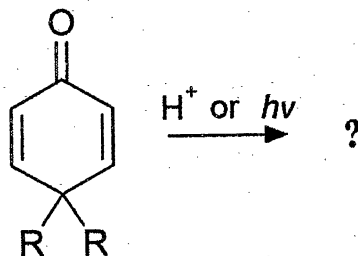
- b Describe the aromaticity of heterocyclic compounds with suitable examples.

- 8 a Write a short note on Stork-enamine reaction.

OR

- b Illustrate the orientation and reactivity of disubstituted benzene with suitable examples.

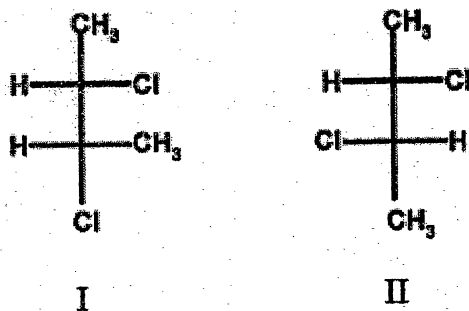
- 9 a Identify the product and outline the mechanism of the following reaction, name the rearrangement.



OR

- b Name the catalyst which is used to convert a ketone into an ester. Name the reaction and outline the mechanism involved in it.

- 10 a How are the projections I and II related to each other? Justify your answer by giving suitable explanations.



OR

- b i) Draw the most stable conformation of cis-1,2-dimethylcyclohexane. (1)
ii) Provide a representation for the gauche conformer of butane. (2)

SECTION -C (30 Marks)

Answer ALL questions

ALL questions carry EQUAL Marks

(5 x 6 = 30)

- 11 a Justify the following statements. (4 x 1.5)

- Chloroacetic acid is stronger than acetic acid.
- Although *o*- and *p*-nitro phenols have the same mol. weight (139) yet the former boils at a very low temperature (44 °C) as compared to the latter which boils at 114 °C.
- The mol. weight of H₂S is 34 and that of H₂O is 18, yet the former is a gas whereas the later is a liquid.
- ter*-Butyl carbonium cation is more stable than the ethyl carbonium cation.

OR

- b Arrive at the equations governing with

- Linear free energy relationships. (3)
- Structure activity relationships of the aliphatic compounds. (3)

Cont...

- 12 a Explain the effect of aromaticity on bond length, resonance energies and induced ring currents.

OR

- b Describe the term aromaticity. Discuss how the aromatic character of cyclopentadienyl anion, tropylium cation and [10]annulene have been explained?

- 13 a Demonstrate the mechanism of S_Ei reaction. How does it compare with S_E2 mechanism? (4+2)

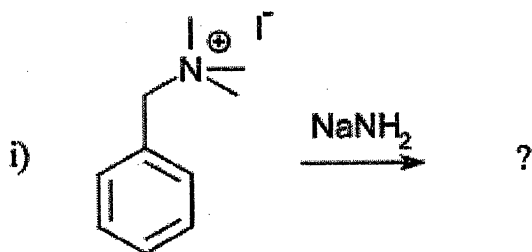
OR

- b How will you carry out the following transformations using Friedel-Craft reaction? (3+3)

i) Benzene \longrightarrow *n*-Propylbenzene

ii) Toluene \longrightarrow 1,2,3-Trimethylbenzene

- 14 a Write the product(s) of the following reactions and explain their mechanisms. (3+3)



OR

- b Explain the mechanism of Damzenov rearrangement and Benzidine rearrangement.

- 15 a Elaborate the optical isomerism of biphenyls and spiranes with adequate examples.

OR

- b Describe the principle and categories of asymmetric synthesis.

Z-Z-Z

END