- (a) Write short notes (Any three)
 - (i) Benzoin condensation
 - (ii) Beckmann rearrangement
 - (iii) Alkaline ester hydrolysis
 - (iv) Thorpe nitrile condensation
 - (b) Write the final product formed in reduction of nitrobenzene under the following conditions:
 - (i) Sn/HCl
 - (ii) Zn/NH₄C1
 - (iii) Electrolytic reduction

(4,4,4,3)

[This question, paper contains 8 printed pages.]

Sr. No of Question Paper: 1564

G

Unique Paper Code

: 2172012302

Name of the Paper

: DSC: Carbonyls, Carboxylic Acids, Amines, Nitro

Compounds, Nitriles, Isonitriles

and Diazonium Salts

Name of the Course

: B.Sc. (Hons.) Chemistry

Semester

: III

Duration: 3 Hours

Maximum Marks: 90

Instructions for Candidates

- Write your Roll No. on the top immediately on receipt of this question paper.
- Attempt six questions in all.
- All questions carry equal marks.
- 1. (a) An organic compound $A(C_5H_8O_2)$ forms a dioxime. It gives a positive Tollen's test. On Clemmensen reduction, it forms n-pentane. It also gives a positive iodoform test to form sodium salt of

dicarboxylic acid which on acidification gives a dicarboxylic acid B $(C_4H_6O_4)$.

- (i) Predict the structures of A and B.
- (ii) Give the reagent used in Clemmensen reduction.
- (iii) Give the reaction involved in the Iodoform test of A to form B.
- (iv) What is the chief use of Tollen's test?
- (b) An optimum pH is required for the reaction of carbonyl compounds with ammonia derivatives.

 Justify the statement.
- (c) Write the synthesis of the following compounds using Ethyl acetoacetate or Diethylmalonate:
 - (i) Crotonic acid
 - (ii) 5,5-Diethylbarbituric acid
- (d) Why tertiary amines with three different groups attached to nitrogen atom do not show optical activity? Explain by taking a suitable example.

(4,4,4,3)

2. (a) Amine A (C₅H₁₃N) on treatment with methyl iodide followed by silver hydroxide forms compound

- 7. (a) Predict the product and give the name of the reaction involved: (Any six)
 - (i) $CH_3CH=CH-COCH_3 + CH_2(COOEt)_2$ $+ ArN_2^+Cl^- \xrightarrow{aq. NaOH}$
 - (iii) CH₃CH₂CH₂NO₂ (i) NaOH (ii) H₂SO₄/boil
 - (iv) $CH_3CH_2CH_2 \stackrel{+}{N} (CH_3)_2 \xrightarrow{\triangle} A + B$
 - (v) CF₃COOOH
 - (vi) $C_6H_5NH_2 + CHCl_3 + 3 KOH \longrightarrow$
 - (vii) CHO NaOH
 - (b) 1,6-diesters undergo cyclization when treated with sodium ethoxide. Write the name of the reaction and its mechanism. (2×6,3)

- (b) How will you distinguish between ethylamine, diethylamine and triethylamine using Hinsberg's method? Give the reactions involved.
- (c) Outline the preparation of n-propylamine by Gabriel phthalimide synthesis.
- (d) Coupling reactions of diazonium salts do not take place in strongly acidic or strongly alkaline conditions. Explain using suitable structures.

(4,4,4,3)

- 6. (a) Discuss the mechanism of acid-catalysed hydrolysis of nitriles.
 - (b) Give a reaction to distinguish between nitriles and isonitriles.
 - (c) Carry out the following conversions: (Any two)
 - (i) m-Bromotoluene from Toluene
 - (ii) o-Chlorophenol from Chlorobenzene
 - (iii) Adipic acid from Diethylmalonate
 - (d) How do primary, secondary and tertiary nitroalkanes react with nitrous acid. Give the reactions involved. (4,4,4,3)

B (C₆H₁₇NO) which is basic in nature. Compound B on heating forms 1-Propene and amine C (C₃H₉N). Identify A, B and C. Give the mechanism of formation of both products from B.

(b) Arrange the following in order of decreasing reactivity towards nucleophilic addition reactions, giving reasons:

CH₃COCH₃; C₆H₅COCH₃; HCHO; CH₃COCH(CH₃)₂

- (c) How will you distinguish between the following compounds on the basis of the product they form on heating:
 - (i) Oxalic acid and Succinic acid
 - (ii) β-Hydroxy acid and Υ-Hydroxy acid
- (d) Write the mechanism of Keto-enol tautomerism in an acidic OR alkaline medium. (4,4,4,3)

3. (a) Elaborate:

- (i) p-Hydroxybenzaldehyde does not undergo Cannizzaro reaction.
- (ii) Benzil rearranges to Benzilic acid when treated with a base. Justify on the basis of reaction mechanism.

(b) Outline the synthesis of the given alkene using Wittig reaction:

(c) Give the product formed and the mechanism involved in the aldol condensation of the given carbonyl compound:

(d) Complete the following reactions:

4. (a) Complete the following sequence of reactions giving structures of A, B, and C. Also give the name of reactions involved in the two sequences:

- (b) What happens when Acetone is reacted with Ethyl bromoacetate in presence of Zinc. Give the name of reaction along with the mechanism.
- (c) All ortho substituted benzoic acids are stronger acids than benzoic acid. Give reason.
- (d) Carboxylic acids do not form oxime even though they have c=0 group in their structure. Give reason. (4,4,4,3)
- 5. (a) Arrange the following in increasing order of basicity, give reason to justify your answer:

$${\rm C_6H_8NH_2}\,;\,\,{\rm m\text{-}OCH_3C_6H_4NH_2}\,;\,\,{\rm p\text{-}OCH_3C_6H_4NH_2}$$