2023

CHEMISTRY — **HONOURS**

Paper: CC-8

(Organic Chemistry - 4)

Full Marks: 50

The figures in the margin indicate full marks.

Candidates are required to give their answers in their own words as far as practicable.

Answer question no. 1 and any eight questions from the rest (question nos. 2 to 12).

1. Answer any ten questions:

 1×10

- (a) What is meant by umpolung? Give one example.
- (b) Primary aromatic amines form stable diazonium salts whereas primary aliphatic amines do not. Explain.
- (c) In the structure of aniline, point out the chromophore and auxochrome components.
- (d) Which of the following nucleii have magnetic property?

$$^{12}_{6}$$
C, $^{14}_{7}$ N, $^{16}_{8}$ O, $^{19}_{9}$ F

(e) Write down the product of the following reaction (no mechanism needed)

Ph
$$C = NOH \xrightarrow{conc. H_2SO_4}$$

$$H_3C$$
(E = Isomer)

(f) Write down the reagents required for the following transformation:

$$R^1R^2NH \xrightarrow{?} R^1R^2N - CH_3$$

- (g) What happens to the UV absorption spectrum (λ_{max}) of aniline when HCl is added to it?
- (h) Write down the synthetic equivalents (SE) of the following synthons :

$$\stackrel{\circ}{\mathrm{CH}}_{2}\mathrm{NH}_{2}, \stackrel{\oplus}{\mathrm{CH}}_{2}\mathrm{CH}_{2}\mathrm{OH}$$

- (i) Both $Ph_2C(OH)C(OH)CMe_2$ and Ph(Me)C(OH) C(Me)(OH)Ph give the same ketone on separate treatment with H_2SO_4 . Write down the structure of the product.
- (j) Write down the structure of the compound $C_5H_{11}C1$ which shows two singlets in its 1H NMR spectrum.

(k) Show the reagents for protection and deprotection of -NH2 group of the following compound:

(I)
$$N-H$$
 ? COOH

- 2. (a) How would you distinguish between the members of each of the following pairs by IR spectroscopy?
 - (i) Ethanol and ethylene glycol
 - (ii) Methyl benzoate and phenyl acetate
 - (b) Give the product of the following reaction along with mechanism.

3+2

3. (a) Identify [A], [B], [C] of the following sequence of reactions:

$$\begin{array}{c} O \\ \parallel \\ R \longrightarrow C \longrightarrow OH \end{array} \xrightarrow{SOCl_2} [\mathbf{A}] \xrightarrow{CH_2N_2} [\mathbf{B}] \xrightarrow{1. \operatorname{Ag}_2O(\operatorname{moist})/\Delta} [\mathbf{C}]$$

Give mechanism for the conversion of [B] to [C].

(b) Give the products of the following reaction and explain their formation.

3+2

4. (a)
$$CH_3 / H_2SO_4 \longrightarrow [D]$$
 Anlyd. AlCl₃ / 80°C E

Give the structures of [D] and [E] and write down the mechanism for the conversion of [D] to [E].

- (b) Arrange E-stilbene and Z-stilbene in order of their increasing λ_{max} value and justify. 3+2
- 5. (a) Predict the major product and give plausible mechanism of the following reaction:

$$\begin{array}{c|c} CH_3 & O \\ & \parallel \\ CH_3 & C - C - CH_3 & \xrightarrow{CF_3CO_3H} \\ & CH_3 & \end{array}$$

(b) Give the product of the following reaction along with mechanism:

$$\stackrel{\text{H}}{\longrightarrow}$$

- **6.** (a) Distinguish between the following pair of compounds with the help of spectroscopic method mentioned in the bracket and justify your answer in each case.
 - (i) Cyclopropanone and cyclohexanone (IR)
 - (ii) 1-chloropropane and 2-chloropropane (¹H NMR)
 - (b) Explain why alkyl isonitriles can not be hydrolysed by alkali.

3+2

3+2

7. (a) Predict the product of the reaction below and show the mechanism involved:

$$\begin{array}{c} \text{Me} \\ \text{III}_{\text{IIII}} \\ \text{PhCH}_2 \end{array} \begin{array}{c} \text{Et} \\ \text{NHO-C} \end{array} \begin{array}{c} \text{Ph} \\ \text{OH}/\Delta \end{array}$$

(b) Why is deuterated solvent used to run ¹H NMR samples?

3+2

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(4)

8. (a) Predict the product of the following reaction with plausible mechanism:

- (b) Which of the two regioisomers of dibromoethane will show a 4H,s in its ¹H NMR spectrum and why?
- 9. (a) Give the synthesis along with the retrosynthesis of the following target molecule:

(b) Illustrate the use of acyloin reaction for the synthesis of large rings.

3+2

10. (a) Predict the product(s) of the following reaction with plausible mechanism:

(b) How would you synthesise the following compound using pinacol-pinacolone rearrangement?

- 11. (a) Saturated cyclic ketones usually record three absorption bands in their UV spectra at around 160 nm, 190 nm and 280 nm. Assign them in terms of electronic transition. Predict with proper reasoning which will record the most intense absorption.
 - (b) Predict the product of the following reaction with plausible mechanism:

3+2

3+2

12. (a) Describe the synthesis of the following compound with proper retrosynthetic analysis.

(b) Give the product along with mechanism of the following reaction:

3+2

$$H - N - N = 0$$

$$HCI$$