3 (Sem-4/CBCS) CHE HC2

2022

CHEMISTRY

(Honours)

Paper: CHE-HC-4026

(Organic Chemistry -III)

Full Marks: 60

Time: Three hours

The figures in the margin indicate full marks for the questions.

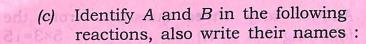
1. Answer any seven from the following:

 $1\times7=7$

- (i) Write the IUPAC nomenclature of pyrrole.
- (ii) What product can you expect if furfural is heated at 200 °C in presence of Pd-C?
- (ii) Write the products of the following:

$$RCH = NO_2Na \xrightarrow{H_2SO_4}$$

- (iv) Name the intermediate compound formed in Hofmann's degradation of amide to amine.
- (v) The rate of electrophilic substitution reactions of heterocyclic compounds is slower than benzene. Why?
- (vi) Why are alkyl isocyanides insoluble in water?
- (vii) Why is naphthalene less aromatic than benzene?
- (viii) How many number of isoprene units are present in citral?
- (ix) Which position of indole is more susceptible to electrophilic substitution?
- (x) Which bond of phenanthrene is readily attacked by reagents?
- 2. Answer **any four** questions from the following: 2×4=8
 - (a) How can 'yellow oil' be prepared from a secondary amine? Give reaction.
 - (b) What happens when $C_6H_5CON_3$ is heated? Write the mechanism of the reaction.



(i)
$$C_2H_5ONO_2 + H_2O \xrightarrow{H} A$$

(ii)
$$CH_3NO_2 + Cl_2 + NaOH \longrightarrow B$$

- (d) Compare the aromaticities of furan and pyrrole and give explanations.
 - (e) Thiophene is less reactive than furan. Explain.
- (f) Compare the basicities of the following:

$$\langle \ddot{N} \rangle$$
 and $\langle \ddot{N} \rangle^N$

Pyrrole

Imidazole

(g) Write the products of the following:

$$C_{10}H_{14}\stackrel{\bigoplus}{N_2}CH_3\stackrel{\bigcirc}{I} \stackrel{\Delta}{\longrightarrow}$$

Nicotine methiodide

(h) What do you mean by isoprene rule?

- 3. Answer **any three** questions from the following: (A to H) 5×3=15
 - A. (a) Explain why aniline cannot undergo 1+1=2
 - (i) Friedel-Craft reaction
 - (ii) Nitration reaction with HNO3
 - (b) Discuss about kinetically and thermodynamically controlled product of napthalene, when it undergoes sulphonation reaction with conc. H_2SO_4 at $80^{\circ}C$ and $160^{\circ}C$.
 - B. (a) Identify A, B, C, D and E in the following: 2½

$$H_3C \xrightarrow{(i) \ HNO_3, \ H_2SO_4} A \xrightarrow{Ac_2O}$$

$$B \xrightarrow{Br_2} C \xrightarrow{NaOH} D \xrightarrow{NaNO_2, HCl} E$$

(b) Identify P and propose a mechanism:

21/2

- C. (a) Write the sequence of reactions involved in the Fischer indole synthesis.
 - (b) Why is catalytic reduction of thiophene difficult?
 - (c) Compare and explain the basicity of indole and quinoline. 2
- D. (a) Find the product of the following reactions:

$$\begin{array}{ccc}
& Cl & \frac{NaNH_2}{liq NH_3} A & \longrightarrow B
\end{array}$$

- (b) Compare the basicities of 2-methyl pyridine and 3-methyl pyridine.
- (c) Write the product P:

$$HC \equiv CH + NH_3 + H_3CO - CH_2 - OCH_3 \frac{Al_2O_3}{500^{\circ}C} P$$

E. (a) Write the mechanism of diazotization of an aromatic amine.

1

- (b) Can you prepare secondary amines using Gabriel's phthalimide synthesis? Give reasons.
 - F. (a) Write the reactions involved in Haworth synthesis of naphthalene.
 - (b) Identify A, B, C and D in the following reactions:

(i)
$$CH_3 CrO_3 A CH_3COOH$$

3

(ii)
$$\overbrace{EtOH}^{Na} \xrightarrow{EtOH} B$$

(iii)
$$2 \bigcirc CH_2Cl$$
 $AlCl_3 \rightarrow C$

(iv)
$$Na/C_2H_5OH \rightarrow D$$

- G (a) Write the reaction mechanism of synthesis of pyrrole by Hantzsch method.
 - (b) Find the product of the following reaction:

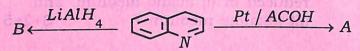
$$\begin{array}{c|c}
\hline
N & CHCl_3, KOH \\
H & H
\end{array}$$

- H. How will you distinguish 1°, 2° and 3° nitroalkanes? What products are obtained when nitrobenzene is reduced in (i) acidic medium, and (ii) alkaline medium? 3+2=5
- 4. Answer **any three** questions from the following A to H: 10×3=30
 - A. (a) How will you ascertain the nature of oxygen and number of double bonds in citral? 1½+1½=3
 - (b) Write different steps involved in the synthesis of citral from acetone and acetylene. 5
 - (c) Write the product and name it:

$$CHO \xrightarrow{K_2CO_3, H_2PO} ?$$

B. (a) Write the sequence of reactions that takes place in the synthesis of quinoline by Doebner-Miller method.

- (b) Find the products of the following:
- 2



Also name the products.

- (c) Which position of quinoline is more susceptible to undergo electrophilic substitution reaction? Explain with proper reasoning.
 - C. (a) Write the method of synthesis of α -terpineol from p-toluidic acid.
 - (b) Write the products when α-terpineol undergoes following series of oxidation reaction:

$$\begin{array}{c} \alpha-terpineol \xrightarrow{KMnO_4} I \xrightarrow{CrO_3} II \\ \xrightarrow{-H_2O} III \xrightarrow{KMnO_4} IV \end{array}$$

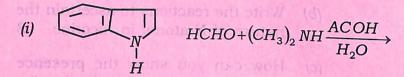
(c) What conclusion can you draw from the above oxidation reactions?

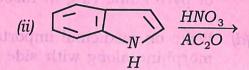
- D. (a) Write how alkaloids can be extracted from plants. 2
 - (b) Write the reactions to ascertain the nature of N-atoms in nicotine. 3
 - (c) How can you show the presence of pyrrolidine ring in nicotine?
 - (d) Write on medicinal importance of morphine along with side effects.
- E. (a) Write different resonating structures of isoquinoline. 2
 - (b) Suggest mechanism of Bischler-Napieralskiol synthesis of isoquinoline. 4
 - (c) Find the final products of the following reaction.

$$\begin{array}{c}
\stackrel{KMnO_4}{\longrightarrow} \\
\stackrel{(O)}{\longrightarrow}
\end{array}$$

(d) Compare the basicities of isoquinoline with pyridine. 2

F. Write the products of the following reactions: 2×5=10





(iii)
$$\bigcap_{N}$$
 $CrO_3 \rightarrow$

(iv)
$$CH_3COCI$$

$$(v) \qquad \bigodot \frac{Ar \, N_2 \, Cl}{NaOH}$$

- G. (a) Compare the basicities of furan, pyrrole and thiophene with proper explanations.
 - (b) Furan is less reactive than pyrrole. Explain. 2

(c) Find the products of the following reactions: 1×5=5

$$(i) \qquad \begin{array}{c} CN \\ \downarrow \\ S \end{array} + \begin{array}{c} CN \\ \downarrow \\ C \\ \downarrow \\ CN \end{array}$$

(ii)
$$\bigcirc$$
 + \bigcirc \bigcirc \bigcirc (i) \bigcirc AlC 1_3 (ii) \bigcirc Zn dust

(iii)
$$\bigcirc$$
 + CH_3COCl \longrightarrow

$$(iv) \quad \bigotimes^{\oplus} \stackrel{\ominus}{N_2Cl} \quad \xrightarrow{OH}$$

$$(v) \qquad \bigvee_{N} \stackrel{(1)}{\underbrace{RLi, H^{+}}}$$

