- H. (a) What is Hoffmann's exhaustive methylation?
 - (b) Apply Hoffmann's exhaustive methylation and Emde's degradation to the following compound to get the final product:



Isoquinoline

- (c) What are different products you can expect when nicotine zinc chloride is distilled?
- (d) Find all the products of the following reaction: 1½

$$CHO \qquad O_3 \longrightarrow$$

(e) What are the therapeutic uses of reserpine?

Total number of printed pages–12

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.

Answer **any seven** from the following: $1 \times 7 = 7$

- (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:

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

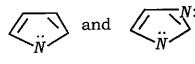
- (iv) Name the intermediate compound formed in Hofmann's degradation of amide to amine.
- (v) The rate of electrophilic substitution reactions of heterocyclic compounds is slower than benzene. Why?
- (vi) Why are alkyl isocyanides insoluble in water?
- (vii) Why is naphthalene less aromatic than benzene?
- (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.

(c) Identify A and B in the following reactions, also write their names:

(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:



Pyrrole

Imidazole

(g) Write the products of the following:

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

$$\underset{H_3C}{\overbrace{\hspace{1cm}(i)\hspace{1cm}HNO_3,\hspace{1cm}H_2SO_4}} A \xrightarrow{\hspace{1cm}Ac_2O}$$

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

(b) Identify P and propose a mechanism:

$$+ MeOOC - C \equiv C - COOMe \longrightarrow P$$

$$2\frac{1}{2}$$

- 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:

$$\underbrace{\bigcap_{N} Cl} \qquad \underbrace{\frac{NaNH_2}{liq NH_3}} A \xrightarrow{\mathcal{D}} B$$

- (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.

- (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)
$$CH_3 CrO_3 A$$

$$CH_3COOH A$$

3

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

(iii)
$$2 \underbrace{CH_2Cl}_{CH_2Cl} \xrightarrow{AlCl_3} C$$

(iv)
$$\sim \frac{Na/C_2H_5OH}{D}$$

- G (a) Write the reaction mechanism of synthesis of pyrrole by Hantzsch method.
 - (b) Find the product of the following reaction: 2

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

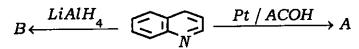
- H. How will you distinguish 1°, 2° and 3° nitroalkanes? What products are obtained when nitrobenzene is reduced in (i) acidic medium, and (ii) alkaline medium? 3+2=5
- 4. Answer **any three** questions from the following A to H: 10×3=30
 - A. (a) How will you ascertain the nature of oxygen and number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

3



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:

(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. 2

$$\overbrace{(O)}^{KMnO_4}$$

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

F. Write the products of the following reactions: $2 \times 5 = 10$

(i)
$$HCHO + (CH_3)_2 NH \xrightarrow{ACOH} H_2O$$

(ii)
$$\overbrace{ | N \rangle \atop H} \xrightarrow{HNO_3} \underbrace{AC_2O}$$

(iii)
$$\stackrel{CrO_3}{ }$$

(iv)
$$CH_3COCI$$

$$(v) \qquad \bigcirc \stackrel{\oplus}{10} \stackrel{\ominus}{\underbrace{NaOH}} \stackrel{}{\longrightarrow}$$

- 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)
$$CN$$

$$CN$$

$$C \longrightarrow C$$

$$C$$

$$C$$

$$C$$

$$C$$

$$C$$

$$C$$

$$C$$

$$C$$

$$C$$

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

$$(iv) \quad \bigcirc \stackrel{\oplus \quad \ominus}{ } \stackrel{\bigcirc}{ } \stackrel{ }{ }$$

$$(v) \qquad \bigvee_{N} \stackrel{(1)}{\overbrace{(2)}} \stackrel{RLi, H^{+}}{\underbrace{(2)}} \stackrel{(2)}{\overbrace{[O]}}$$