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:

 $1 \times 7 = 7$

- (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:

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

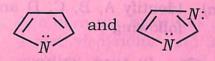
- (iv) Name the intermediate compound formed in Hofmann's degradation of amide to amine.
 - (v) The rate of electrophilic substitution reactions of heterocyclic compounds is slower than benzene. Why?
 - (vi) Why are alkyl isocyanides insoluble in water?
 - (vii) Why is naphthalene less aromatic than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

$$C_{10}H_{14}\overset{\bigoplus}{N_2}CH_3\overset{\bigcirc}{I} \xrightarrow{\Delta}$$

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. H₂SO₄ at 80°C and 160°C.
 - B. (a) Identify A, B, C, D and E in the following: $2^{1/2}$

$$H_3C$$
 (i) HNO_3 , H_2SO_4 A Ac_2O (ii) $H_2/Pd-C$ A

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

(b) Identify P and propose a mechanism:

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:

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

(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)
$$CH_3 CrO_3 A CH_3COOH$$

- (ii) $\overbrace{EtOH}^{Na} \xrightarrow{B}$
- (iii) $2 \bigcirc CH_2Cl$ $AlCl_3 \rightarrow C$
- (iv) Na/C_2H_5OH
- G (a) Write the reaction mechanism of synthesis of pyrrole by Hantzsch method.
 - (b) Find the product of the following reaction:

- 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:
- $B \leftarrow \underbrace{LiAlH_4}_{N} \qquad \underbrace{Pt / ACOH}_{N} A$

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:

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

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

(d) Compare the basicities of isoquinoline with pyridine.

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- F. Write the products of the following reactions: $2 \times 5 = 10$
- $HCHO + (CH_3)_2 NH \frac{ACOH}{H_2O}$

(ii)
$$\underbrace{HNO_3}_{AC_2O} \xrightarrow{HNO_3}$$

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

Find the products of the following reactions: $1 \times 5 = 5$

(i)
$$CN$$

$$C \longrightarrow C$$

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

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

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

- 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: $1^{1/2}$

$$CHO$$
 O_3

(e) What are the therapeutic uses of reserpine?