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: 1×7=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:

$$RCH = \stackrel{\ominus}{NO_2Na} \stackrel{H_2SO_4}{\longrightarrow}$$

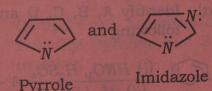
- (iv) Name the intermediate compound formed in Hofmann's degradation of amide to amine.
- The rate of electrophilic substitution reactions of heterocyclic compounds is slower than benzene. Why?
- (vi) Why are alkyl isocyanides insoluble in water?
- (vii) Why is naphthalene less aromatic than benzene?
- (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?
- Answer any four questions from the $2 \times 4 = 8$ following:
 - (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.
- Compare the basicities of the following:



Write the products of the following:

$$C_{10}H_{14}N_{2}CH_{3}I \xrightarrow{\Delta}$$
Vicating methodide

Nicotine methiodide

What do you mean by isoprene rule?

- Answer any three questions from the following: (A to H) 5×3=15
 - (a) Explain why aniline cannot 1+1=2 undergo
 - (i) Friedel-Craft reaction
 - Nitration reaction with HNO3
 - Discuss about kinetically and thermodynamically controlled product of napthalene, when it undergoes sulphonation reaction with conc. H2SO4 at 80°C and 160°C.
 - Identify A, B, C, D and E in the B. 21/2 following:

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

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

Identify P and propose a mechanism:

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

$$\begin{array}{c|c}
Cl & \frac{NaNH_2}{liq NH_3} A \xrightarrow{\mathcal{D}} B
\end{array}$$

- Compare the basicities of 2-methyl pyridine and 3-methyl pyridine.
- Write the product P:

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

(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) CH₃ CrO₃ A

 (ii) CH₃COOH

 (iii) Na

 EtOH

 CH_CL

(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:

- 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:

$$CHO$$

$$K_2CO_3, H_2PO$$

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:
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$$B \leftarrow \underbrace{LiAlH_4}_{A} \quad \boxed{\bigcirc I_N} \xrightarrow{Pt / ACOH} A$$

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: 4

$$\alpha-terpineol \xrightarrow{KMnO_4} I \xrightarrow{CrO_3} II$$

$$CH_3 COOH$$

$$\xrightarrow{-H_2O} III \xrightarrow{KMnO_4} IV$$

(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.

$$\begin{array}{c}
\text{EVE}_{N} & \frac{KMnO_{4}}{(O)}
\end{array}$$

(d) Compare the basicities of isoquinoline with pyridine.

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F. Write the products of the following reactions:

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

(ii)
$$\frac{HNO_3}{AC_2O}$$

(iv)
$$CH_3COCI$$

$$(v) \qquad \overbrace{\qquad \qquad } \stackrel{\bigoplus}{NaOH} \stackrel{\ominus}{\longrightarrow}$$

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

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

(ii)
$$\bigcirc$$
 + 0 \bigcirc (i) AlC l_3 (ii) Zn dust

$$(iv) \quad \bigotimes^{\oplus} \stackrel{\Theta}{\underset{N_2Cl}{\bigvee}} \quad \stackrel{\bigcirc}{\underset{}} \stackrel{OH}{\underset{}}$$

$$(v) \qquad \bigvee_{N} \stackrel{(1)}{(2)} \stackrel{RLi, H^+}{(2)}$$

- (a) What is Hoffmann's exhaustive H. 2 methylation?
 - Apply Hoffmann's exhaustive (b) methylation and Emde's degradation to the following compound to get the final product:



Isoquinoline

- What are different products you (c) can expect when nicotine zinc chloride is distilled? 11/2
- (d) Find all the products of the following reaction: 11/2

$$CHO O_3$$

What are the therapeutic uses of reserpine?

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