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 :

$$RCH = \overset{\ominus}{N}O_2\overset{\oplus}{N}a \xrightarrow{H_2SO_4}$$

(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 :

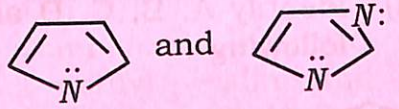
(i) $C_2H_5ONO_2 + H_2O \xrightarrow{H^{\oplus}} A$

(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 :

$C_{10}H_{14}\overset{\oplus}{N}_2CH_3\overset{\ominus}{I} \xrightarrow{\Delta}$

Nicotine methiodide

(h) What do you mean by isoprene rule ?

Contd.

3. Answer ***any three*** questions from the following : (A to H) 5×3=15

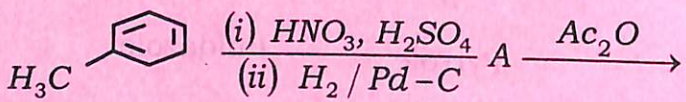
A. *(a)* Explain why aniline cannot undergo 1+1=2

(i) Friedel-Craft reaction

(ii) Nitration reaction with HNO_3

(b) Discuss about kinetically and thermodynamically controlled product of napthalene, when it undergoes sulphonation reaction with conc. H_2SO_4 at 80°C and 160°C. 3

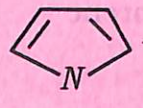
B. *(a)* Identify A, B, C, D and E in the following : 2½



$$H_3C \xrightarrow[(ii)\ H_2/Pd-C]{(i)\ HNO_3,\ H_2SO_4} A \xrightarrow{Ac_2O}$$

$$B \xrightarrow{Br_2} C \xrightarrow[\Delta]{NaOH} D \xrightarrow[H_3PO_2]{NaNO_2,HCl} E$$

(b) Identify *P* and propose a mechanism :



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

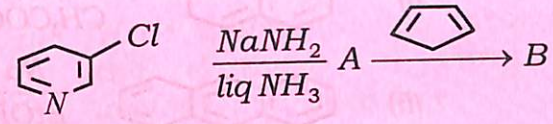
2½

C. *(a)* Write the sequence of reactions involved in the Fischer indole synthesis. 2

(b) Why is catalytic reduction of thiophene difficult ? 1

(c) Compare and explain the basicity of indole and quinoline. 2

D. *(a)* Find the product of the following reactions : 2



$$\xrightarrow[liq\ NH_3]{NaNH_2} A \xrightarrow{} B$$

(b) Compare the basicities of 2-methyl pyridine and 3-methyl pyridine. 2

(c) Write the product *P* : 1

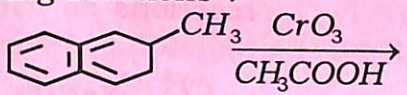
$$HC\equiv CH + NH_3 + H_3CO-CH_2-OCH_3 \xrightarrow[500°C]{Al_2O_3} P$$

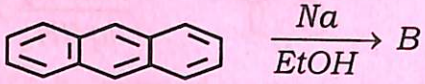
E. *(a)* Write the mechanism of diazotization of an aromatic amine. 3

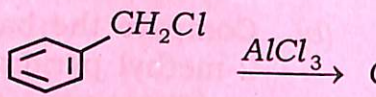
(b) Can you prepare secondary amines using Gabriel's phthalimide synthesis ? Give reasons. 2

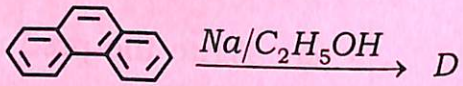
F. (a) Write the reactions involved in Haworth synthesis of naphthalene. 3

(b) Identify A, B, C and D in the following reactions : 2

(i) 

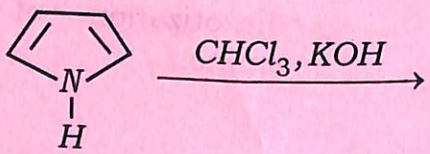
(ii) 

(iii) 

(iv) 

G (a) Write the reaction mechanism of synthesis of pyrrole by Hantzsch method. 3

(b) Find the product of the following reaction : 2



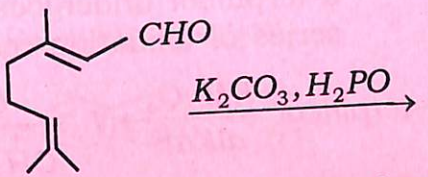
H. How will you distinguish 1°, 2° and 3° nitroalkanes ? What products are obtained when nitrobenzene is reduced in (i) acidic medium, and (ii) alkaline medium ? 3+2=5

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

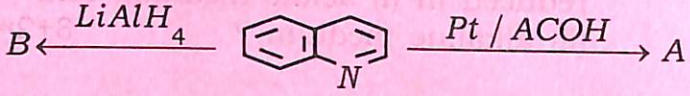
(b) Write different steps involved in the synthesis of citral from acetone and acetylene. 5

(c) Write the product and name it : 2



B. (a) Write the sequence of reactions that takes place in the synthesis of quinoline by Doebner-Miller method. 5

(b) Find the products of the following : 2

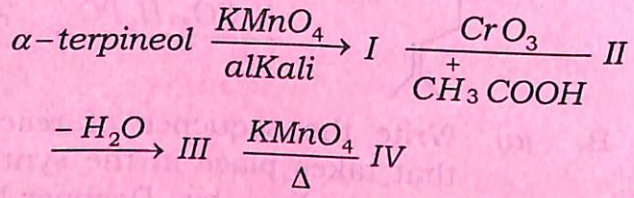


Also name the products.

(c) Which position of quinoline is more susceptible to undergo electrophilic substitution reaction ? Explain with proper reasoning. 3

C. (a) Write the method of synthesis of α-terpineol from *p*-toluidic acid. 4

(b) Write the products when α-terpineol undergoes following series of oxidation reaction : 4



(c) What conclusion can you draw from the above oxidation reactions ? 2

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

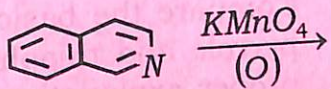
(c) How can you show the presence of pyrrolidine ring in nicotine ? 4

(d) Write on medicinal importance of morphine along with side effects. 1

E. (a) Write different resonating structures of isoquinoline. 2

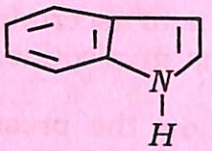
(b) Suggest mechanism of Bischler-Napieralskiol synthesis of isoquinoline. 4

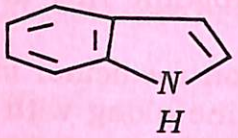
(c) Find the final products of the following reaction. 2



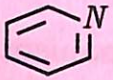
(d) Compare the basicities of isoquinoline with pyridine. 2

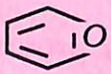
F. Write the products of the following reactions : 2×5=10

(i)  $\xrightarrow[H_2O]{HCHO+(CH_3)_2NH\ ACOH}$

(ii)  $\xrightarrow[AC_2O]{HNO_3}$

(iii)  $\xrightarrow{CrO_3}$

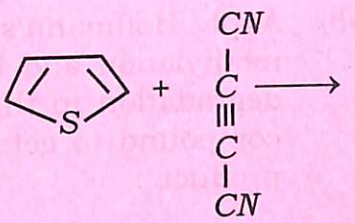
(iv)  $\xrightarrow{CH_3COCl}$

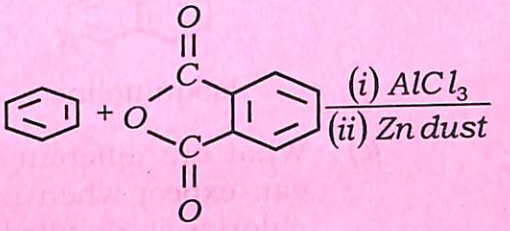
(v)  $\xrightarrow[NaOH]{Ar\overset{\oplus}{N_2}Cl^{\ominus}}$

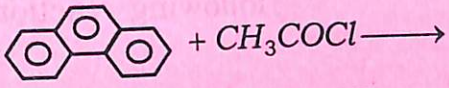
G. (a) Compare the basicities of furan, pyrrole and thiophene with proper explanations. 3

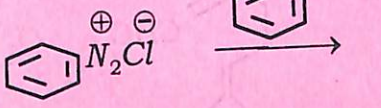
(b) Furan is less reactive than pyrrole. Explain. 2

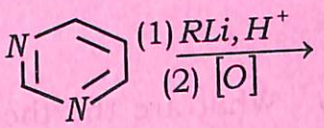
(c) Find the products of the following reactions : 1×5=5

(i) 

(ii) 

(iii) 

(iv) 

(v) 

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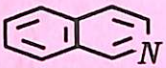
H. *(a)* What is Hoffmann's exhaustive methylation ? 2

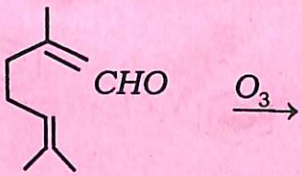
(b) Apply Hoffmann's exhaustive methylation and Emde's degradation to the following compound to get the final product : 4



Isoquinoline

(c) What are different products you can expect when nicotine zinc chloride is distilled ? 1½

(d) Find all the products of the following reaction : 1½



(e) What are the therapeutic uses of reserpine ? 1