Total No. of Questions—12] [Total No. of Printed Pages—8+4

[3762]-171

S.E. (Chemical) (I Sem.) EXAMINATION, 2010

CHEMISTRY—I

(2008 COURSE)

Time : Three Hours **Maximum Marks : 100**

N.B. :— (*i*) Answer any *three* questions from Section I and any *three* questions from Section II.

(*ii*) Answers to the two Sections should be written in separate answer books.

(*iii*) Neat diagrams must be drawn wherever necessary.

(*iv*) Use of logarithmic tables, slide rule, Mollier charts, electronic pocket calculator and steam tables is allowed.

(*v*) Assume suitable data, if necessary.

SECTION I

1. (*a*) What is LCAO approximation ? Draw the MO diagram for nitrogen molecule. [6]

(*b*) Draw the resonating structures for the following :

(*i*) Phenol

(*ii*) Phenoxide ion

(*iii*) P-nitroaniline. [6]

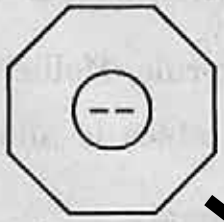
P.T.O.

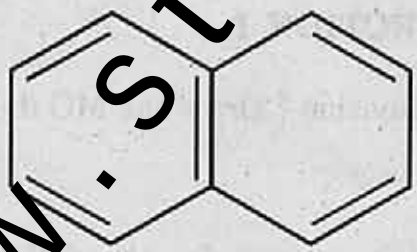
(*c*) Discuss the structure of a carbocation, carbanion and free radical. [6]

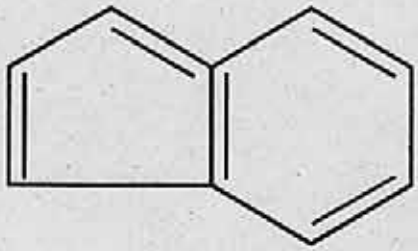
Or

2. (*a*) What is aromaticity ? Using Hückel's rule explain the aromaticity of the following compounds : [6]

(*i*) 

(*ii*) 

(*iii*) 

(*iv*) 

(b) What is the effect of resonance and inductive effect on pKa values of acids and bases ? [6]

(c) Discuss the following with examples :

(i) Electrophiles

(ii) Free radicals

(iii) Elimination reactions. [6]

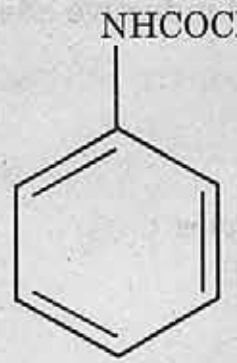
3. (a) What are the factors favouring SN^1 and SN^2 reactions ? Describe the effect of solvent and effect of leaving group on the reactions. [6]

(b) Write the mechanism involved in Friedel-Craft's alkylation and acylation reactions. [6]

(c) Complete the following reactions :

(i) $CH_3 - CH_2OCH_3 \xrightarrow[\text{Methoxide}]{\text{Sodium}}$

(ii) $CH_3 - \underset{\displaystyle CH_3}{\underset{|}{CHOH}} - CH_3 \underset{90°C}{\overset{20\%\ H_2SO_4}{\rightleftharpoons}}$

(*iii*) 

$\xrightarrow{\text{Sulphonation}}$

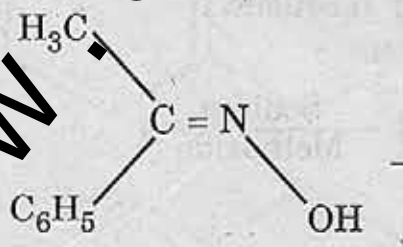
(*iv*) $CH_3Br + RNH_2 \rightarrow$. [4]

Or

4. (*a*) Explain why chlorine acts as ortho-para deactivating when it is present on a benzene ring undergoing electrophilic substitution. [6]

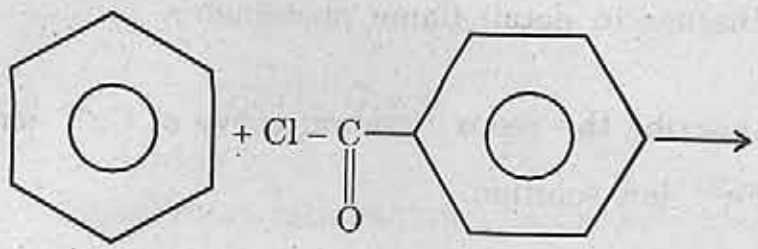
(*b*) Give the mechanism of Claisen's rearrangement. [4]

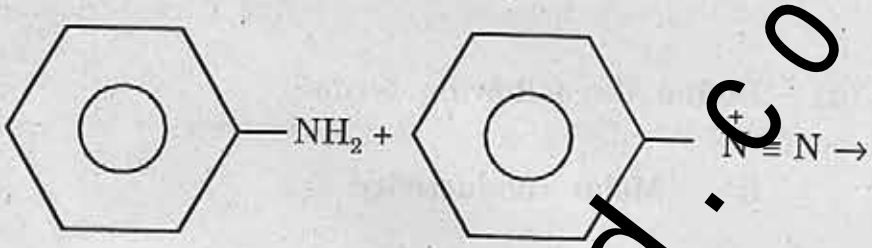
(*c*) Predict the product :

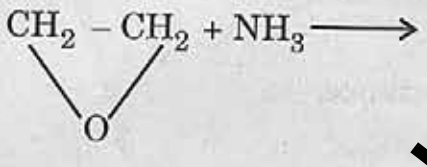
(*i*) 

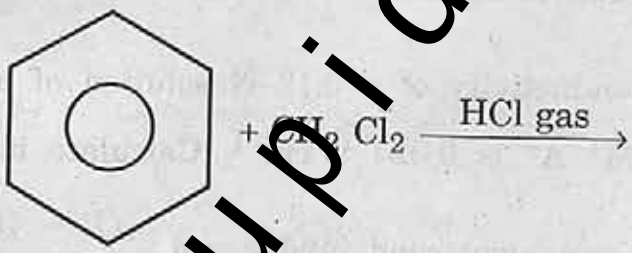
$\xrightarrow{\text{Catalyst}}$

(*ii*) $CH_3 - CH = CH_2 \xrightarrow[H^+]{H_2O}$

(iii) 

(iv) 

(v) 

(vi) 

[6]

5. (a) What is Kohlrausch's law ? Calculate the molar conductivity at infinite dilution $\left(\Lambda_m^\infty\right)$ for NH_4OH for the following data :

Λ_m^∞ $(Ba(OH)_2)$ = 523.3 S cm^2 mol^{-1};

$\Lambda_m(BaCl_2)$ = 280.0 S cm^2 mol^{-1};

Λ_m^∞ (NH_4Cl) = 129.8 S cm^2 mol^{-1}. [4]

(b) Discuss in detail flame photometry. [6]

(c) Describe the redox titration curve of Ce^{4+} ion solution against Fe^{2+} ion solution. [6]

Or

6. (a) Define the following terms :

(i) Molar conductivity.

(ii) Equivalent conductivity.

(iii) Specific conductance.

(iv) Cell constant.

The conductivity of a 0.12 N solution of an electrolyte of the type $M^+ A^-$ is 0.024 $S\ cm^{-1}$. Calculate its :

(i) equivalent conductivity and

(ii) molar conductivity. [6]

(b) Write short notes on :

(i) Gas sensing electrode.

(ii) Enzyme based electrode. [6]

(c) What is a titration curve ? Discuss the titration curve for the neutralization of a strong acid with a weak base. [4]

SECTION II

7. (*a*) Derive the integrated rate equation for second-order kinetics for two reactants with same initial concentrations. [6]

(*b*) Rate law for decomposition of N_2O_5, $N_2O_5 \rightarrow 2NO_2 + \frac{1}{2} O_2$ is observed

$$R = \frac{-d[N_2O_5]}{dt} = K[N_2O_5]$$

(*i*) $N_2O_5 \underset{}{\overset{K}{\rightleftharpoons}} NO_2 + NO_3$ (fast)

(*ii*) $NO_2 + NO_3 \xrightarrow{K_1} NO_2 + NO + O_2$ (slow)

(*iii*) $NO + NO_3 \xrightarrow{K_2} 2NO_2$ (fast)

show that rate law is consistent to mechanism proposed. Find S.S.A. for each unstable intermediates involved. [6]

(*c*) Discuss the Stark-Einstein law of photochemical equivalence. [4]

Or

8. (*a*) Derive the integrated rate equation for second order kinetics for two reactants with different initial concentrations. [6]

(*b*) For the reaction, $2NO + Cl_2 \rightarrow 2NOCl$, the data obtained are :

Experiment	$[Cl_2]_0$, mol L^{-1}	$[NO]_0$, mol L^{-1}	Initial rate mol L^{-1} S^{-1}
I	0.02	0.01	2.40×10^{-4}
II	0.02	0.03	2.16×10^{-3}
III	0.04	0.03	4.32×10^{-3}

Determine :

(*i*) Order with respect to Cl_2

(*ii*) Rate law for the reaction

(*iii*) Rate constant. [6]

(*c*) What is activation energy ? How is the rate constant of a reaction related to its activation energy ? [4]

9. (*a*) What are the different types of chromatography ? Describe column chromatography in detail. [6]

(*b*) Write a short note on Nickel-Cadmium battery. [6]

(*c*) Describe the working of any *one* of the detectors used in gas chromatography. [4]

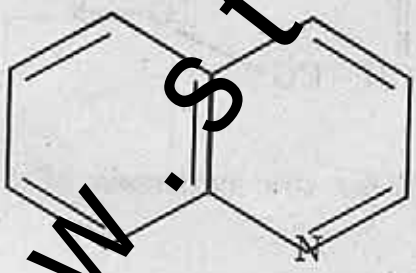
Or

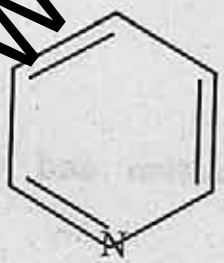
10. (*a*) Discuss in detail the principle, instrumentation and applications of HPLC. [6]

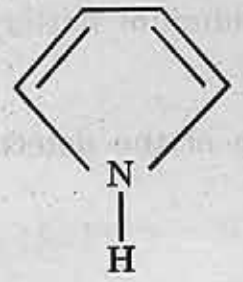
(*b*) What is a fuel cell ? Explain working of H_2-O_2 fuel cell. [6]

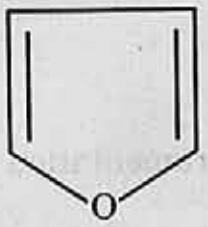
(*c*) Enlist the various applications of chromatography. [4]

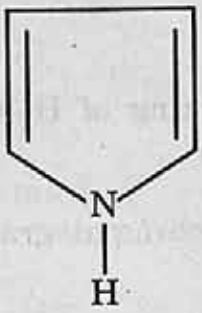
11. (*a*) Complete the following reactions :

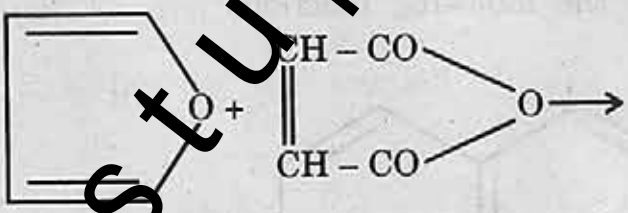
(*i*)  $\xrightarrow{Sn/HCl}$

(*ii*)  $\xrightarrow[320°C]{KOH}$

(iii)  + $\xrightarrow{CHCl_3/KOH}$

(iv)  + $2H_2 \xrightarrow{Pd/H_2}$

(v)  + $\xrightarrow[5°C]{CH_3COO^- NO_2^+}$

(vi) 

[6]

(b) Give *one* method each for the synthesis of :

(i) Pyrrole

(ii) Ominoline

(iii) Pyridine. [6]

(c) Write a short note on diazotization and coupling in azo dyes. [6]

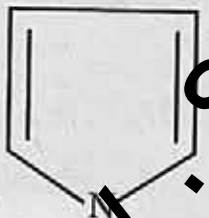
Or

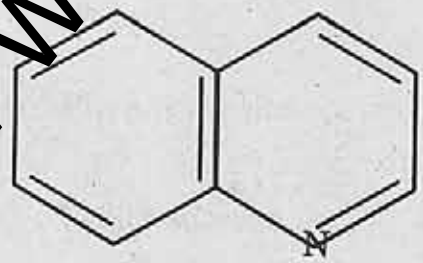
12. (*a*) What are phthalein dyes ? Describe the method of preparation and uses of phenolphthalein dyes. [6]

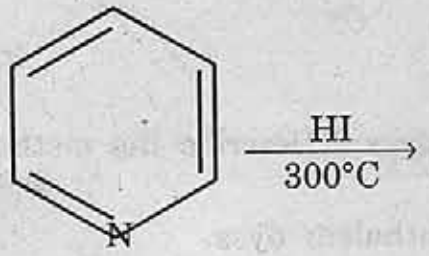
(*b*) Predict the product :

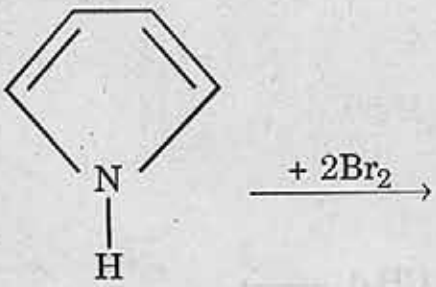
(*i*)  $+ CH_3I \longrightarrow$

(*ii*)  $+ Br_2 \xrightarrow[\text{5°C}]{\text{Dioxan}}$

(*iii*)  $+ 3[O] \xrightarrow[CH_3COOH]{CrO_3}$

(*iv*)  $\xrightarrow{HNO_3/H_2SO_4}$

(v) 

(vi) 

[6]

(c) Give classification of dyes on the basis of application and chemical structure. [6]