2015

CHEMISTRY

(*Organic/Inorganic*)

[**Honours**]

PAPER – III(Gr.-A + B)

Full Marks : 90

Time : 4 hours

The figures in the right hand margin indicate marks

Use seperate scripts for Group-A and Group-B

(*Organic*)

GROUP – A(*a*)

Answer any **one** question

1. (*a*) Explain capatodative radical with an example. $1\frac{1}{2}$

(*b*) What is Hammond's postulate ? How can it be used to explain the following statement :

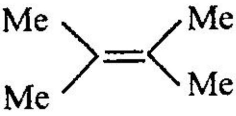
"During radical-induced hologenation of Me_3CH, bromination is more selective (>99% Me_3CBr) than chlorination (33 % Me_3CCl)." 1 + 2

(*c*) Draw an energy-profile diagram of a hypothetical reaction $A \rightleftharpoons B \rightleftharpoons C$ in which the relative stabilities of the three species are $C > A > B$ and for which the relative order of the four rate constants is $k_2 > k_{-1} > k_1 >> k_{-2}$. Which is the rate determining step in your diagram ? 2 + 1

(*d*) Write the mechanism of syn-dihydroxylation of alkene using OsO_4 and also by Woodward's method. These two methods are comple-mentary to each other-justify. $1\frac{1}{2} \times 2 + 1$

(*e*) Phenolysis of optically active α-phenethyl chloride was found to proceed with retention of configuration-explain. 2

(*f*) Which of the following two olefins is more prone towards ozonolysis reaction and why ? $1\frac{1}{2}$



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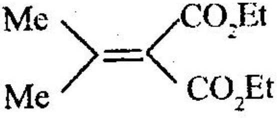


2. (*a*) E^1–E^2– E^1CB is a complete spectrum for 1,2-elimination reaction– Explain the statement taking Saytzeff and Hofmann elimination into account. 3

(*b*) How can you dissolve $KMnO_4$ into benzene to prepare 'purple benzene' ? 1

(*c*) Explain the following reactions with mechanism : $2\frac{1}{2}\times 2$

(*i*) Methyl 2, 4, 6-triphenyl benzoate is dissolved in conc. H_2SO_4 and the resultant solution was poured into water.

(*ii*) t'Butylacetate is heated in methanol in the presence of *p*-toluenesulfonic acid.

(*d*) Bormination of ethyl methyl ketone proceeds differently in (*i*) acid and (*ii*) basic medium. Write the products and explain with mechanism of the reactions. 3

(*e*) Reaction of CH_3CO_2Et with NaOEt gives Claisen condenstion but Me_2CHCO_2Et fails to give under similar conditions-explain showing mechanism of the reaction. 3

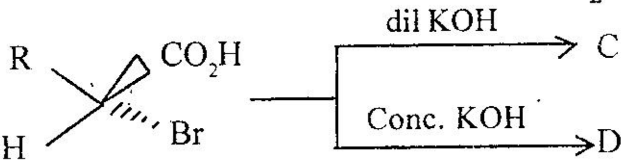
GROUP – A(*b*)

Answer any **two** questions

3. (*a*) Write structures **A** to **D** and explain the reactions with mechanism,

(*i*) $$RCH_2CO_2H \xrightarrow{\text{Red P(cat.)} + Br_2} A$$
$$RCH_2CO_2H \xrightarrow{\text{excess red P} + Br_2} B$$

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

(*ii*) 

1 × 2

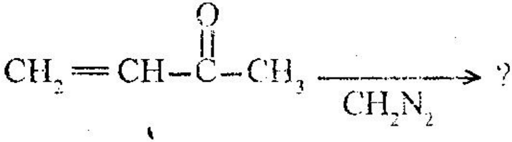
(*b*) *p-N, N*-Dimethylaminobenzaldehyde fails to give benzoin condensation but does when it is used with benzaldehyde under appropriate reaction condition—Explain. Write the mechanism of the cross condensation reaction and mention the corss product. $1 + 1\frac{1}{2} + \frac{1}{2}$

(*c*) How can you find out the preferred site of electrophlic atack on anthracene ? 2

4\. (*a*) Complete the following reactions with proper explanation (any *two*) : 2 × 2

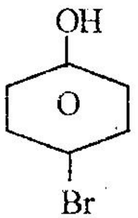
(*i*) $\text{Z-2-Butene} \xrightarrow[\text{in } N_2 \text{ atm.}]{CH_2N_2/h\nu} ?$

(*ii*)



$CH_2{=}CH{-}\overset{\overset{O}{\|}}{C}{-}CH_3 \xrightarrow[CH_2N_2]{} ?$

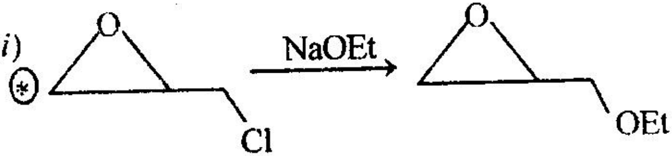
(*iii*)



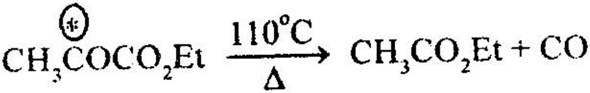
$\xrightarrow[\text{liq } NH_3]{KNH_2} ?$

(*b*) Write the mechanism of the following reaction, assign the position of the labelled carbon in the product structure and write additional products where missing (any *three*) : 3 × 2

(*i*)

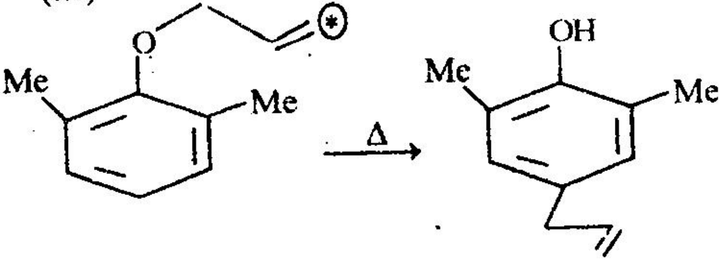


(*ii*)

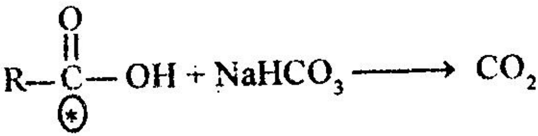


$$\mathrm{CH_3\overset{\circledast}{C}OCO_2Et \xrightarrow[\Delta]{110^{\circ}C} CH_3CO_2Et + CO}$$

(*iii*)



(*iv*)

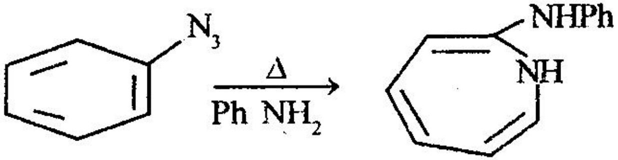


$$\mathrm{R-\overset{\overset{O}{\|}}{\underset{\circledast}{C}}-OH + NaHCO_3 \longrightarrow CO_2}$$

5. (*a*) Explain kinetically and thermodynamically controlled products with reference to sulfonation of naphthalene. 3

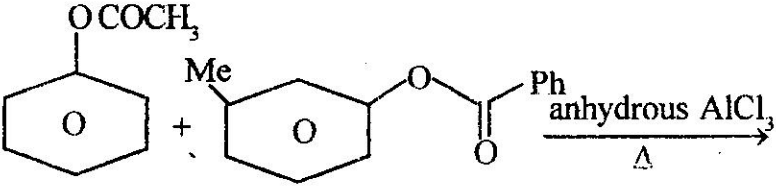
(*b*) Acetolysis of both 4-methoxy-1-pentyl -brosylate and 5-methoxy-2-pentyl brosylate gave same mixture of products—Explain. 2

(*c*) Write down the mechanism of the following reaction : 2

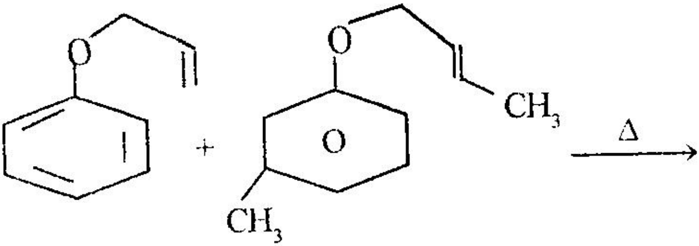


(*d*) Complete the following reactions giving proper explanations : $1\frac{1}{2} \times 2$

(*i*)



(*ii*)



6. (*a*) Outline the preparation of diazomethane from *N*-methyl-*p*-toluenesulfonamide. 2

(*b*) How can you dry an ethereal solution of diazomethane ? 1

(*c*) In Arndt Eistert synthesis 2-equivalents of diazomethane is required —why ? $2\frac{1}{2}$

(*d*) Comment on the base-catalysed hydrolysis of alkyl cyanide and alkyl isocyanide. 2

(*e*) Although aliphatic fluorides are less easily hydrolysed than corresponding chlorides, 2, 4-dinitro fluorobenzene is more readily hydrolysed than 2, 4-dinitro chlorobenzene —Explain. $2\frac{1}{2}$

(*Continued*)

GROUP – A(*c*)

7. Complete the following giving mechanism (any *five*) : 2 × 5

(*i*) $RCH(OH)CO_2Ag + Br_2 \longrightarrow ?$

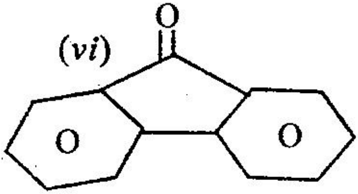
(*ii*) $Me_2C{=}CH_2 \xrightarrow[\text{DCM}]{PhCO_3H} ? \xrightarrow{BF_3\cdot Et_2O} ?$

(*iii*) $CH_3CHO + CH_2O \text{ (excess)} \xrightarrow{\bar{O}H} ?$

(*iv*) $PhCOCH_3 \xrightarrow[\text{Et}_2\text{O, } 0^\circ\text{C}]{Br_2/\text{anhy. } AlCl_3 \text{(cat.)}} ?$

(*v*) $PhCOCH_3 \xrightarrow[80\text{ - }85^\circ\text{C}]{Br_2/\text{anhy. } AlCl_3 (2\cdot 5 \text{ eq.})} ?$

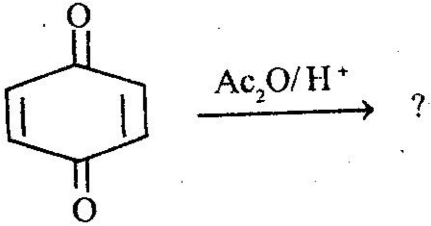
(*vi*)



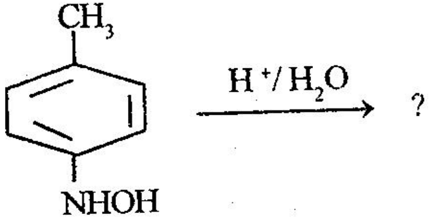
$\xrightarrow[\text{NaOAc}]{NH_2OH \cdot HCl} ? \xrightarrow{H_2SO_4} ?$

(*vii*) $Ph\,N_2^+Cl^- + \overset{\ominus}{C}H\,(CO_2Et)_2 \xrightarrow{\text{NaOAc}} ?$

(*viii*)



(*ix*)



(*Inorganic*)

GROUP – B(*a*)

Answer any **one** question

8. (*a*) An ampule containing 1·0 milli curie of krypton (Kr) gas consisting of a mixture of active isotope Kr^{85} and a stable isotope Kr^{84}. If the volume of the mixture is10 cc at STP and half of Kr^{85} is 10 years, calculate the percentage by weight of Kr^{85} present in the mixture. 5

(Continued)

(*b*) Discuss the origin and physical significance of magnetic quantum numbers. 3

(*c*) Discuss the O–O bond distance in H_2O_2 and O_2F_2 molecules. 2

(*d*) What happens when $AgNO_3$ is added to a solution of $Na_2S_2O_3$. 2

(*e*) What are 'triplet' and 'singlet' dioxygen ? Which one is more reactive and why ? 3

9. (*a*) How did Sommerfield explained the occurance of fine structure in the line spectra of hydrogen atom. 4

(*b*) Explain why 2 × 2

(*i*) $H_2S_2O_7$ is a stronger acid than liquid H_2SO_4.

(*ii*) S – S bond is very weak in $S_2O_4^{2-}$.

(*c*) Compare the bond angles in IF_2^+ and IF_6^+. 3

(*d*) ClO_2 is a free radical with one unpaired electron but it has no tendency to dimenise like NO_2. 2

(*e*) Find out the equivalence point potential during the titration of a 0·1 (M) Fe^{2+} solution with 0.1 (M) Ce^{4+} solution

$E^{\circ}_{Fe^{3+}/Fe^{2+}} = +0\cdot77\,V$ and

$E^{\circ}_{Ce^{4+}/Ce^{3+}} = +1\cdot57\,V$. 2

GROUP – B(*b*)

Answer any **two** questions :

10. (*a*) State de Broglie hypothesis. Show how Bohr's quantum restriction can be attained from it on hydrogen atom orbit. 3

(*b*) C^{14} undergoes a β decay assuming no γ-radiation occurs, calculate the kinetic energy of the electron emitted [Mass of C^{14} = 14·003242 U and N^{14} = 14·003074 U]. 3

(*c*) Compare the acidic and oxidising properties of H_2SO_4 and H_2SeO_4. 4

11. (*a*) The first ionisation energies of boron, carbon, nitrogen, oxygen, fluorene and neon are 800, 1086, 1402, 1313, 1680 and 2080 kJ mol^{-1} respectively. Discuss the observation. 3

(*b*) $BrF_5(l)$ can not be stored in a glass apparatus —Explain. 2

(*c*) Draw a Frost diagram for Hg in acid solution from the given Latimer diagram :

$$Hg^{2+} \xrightarrow{0{\cdot}911\text{ V}} Hg_2^{2+} \xrightarrow{0{\cdot}796\text{ V}} Hg$$

Comment on the tendency of species that undergoes disproportionation. 3

(*d*) When 0·05 moles of NaOH was added to 1 litre of a buffer solution, its pH changes from 5·75 to 5·85. Find the buffer capacity of the resulting mixture. 2

12. (*a*) Out of water and acetic acid, which one will help to determine the relatives strengths of HCl and $HClO_4$? Why ? 3

(*b*) Sodium theosulphate can be oxidised by I_2 in neutral and alkaline media. Compare the equivalent weights of sodium thiosulphate in the above two media. 2

(*c*) Standard potential of Fe'''/Fe'' couple is 0.77V. On treatment with sufficient excess of NH_4HF_2, both Fe''' and Fe'' form hexafluoro complexes. If the Fe''' complex is 10^{10} times more stable than the Fe'' complex, calculate the formal potential of the Fe'''/Fe'' couple under this condition and discuss what would happen on addition of KI into Fe''' solution (*i*) in the absence and (*ii*) in the presence of NH_4HF_2. (Given : Std potential of $I_2/2I^-$ couple is 0·54V). 5

13. (*a*) Give examples of analytical uses of $K_2S_2O_8$ and H_2O_2. 2

(*b*) How will you detect Br^- and I^- ions from thier mixture. Write the related equations. 3

(*c*) From the following Latimer diagram, calculate the reduction potential of $ClO_4^- - HClO$ couple : 3

$$\begin{tikzcd}
ClO_4^- \arrow[r, "+1{\cdot}20V"] & ClO_3^- \arrow[r, "+1{\cdot}18V"] & ClO_2^- \arrow[r, "+1{\cdot}70V"] & HClO \arrow[dl, "+1{\cdot}63V"] \\
 & Cl^- & Cl_2 \arrow[l, "+1{\cdot}36V"'] &
\end{tikzcd}$$

(*d*) What are isodiapheres and mirror nuclei ? Give examples of each. 2

GROUP – B(*c*)

Answer any **five** questions : 2 × 5

14. (*a*) Explain why $SiCl_4$ has a lower boiling point than CCl_4.

(*b*) Compare the basic properties of SCl_4, $SeCl_4$, and $TeCl_4$.

(*c*) Complete the following reaction :

$$RCH = CH_2 + SiHCl_3 \xrightarrow{H_2PtCl_6(\text{cat.})}$$

(*d*) Describe the molecular geometry of XeO_3F_2 on the basis of VSEPR theory.

(*e*) Write the balanced equation for the oxidation of $HXeO_4^-$ by ozone.

(*f*) Show that the oxidising power of $KMnO_4$ depends on the pH of the medium.

(*g*) Show that the disproportionation reaction of H_2O_2 to O_2 and H_2O is spontaneous under acidic condition :

$$O_2 \xrightarrow{+0{\cdot}70V} H_2O_2 \xrightarrow{+1{\cdot}76V} H_2O$$
