This question paper contains **36** printed pages]

H.P.A.S. (Main)—2011

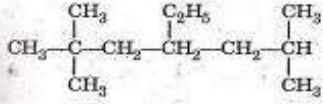
CHEMISTRY

Paper II

Time : 3 *Hours* *Maximum Marks* : 150

Note :— Question No. **1** is compulsory and attempt any other *four* questions out of the remaining seven questions i.e. attempt *five* questions in all. *All* parts of a question must be attempted in continuation at one place.

1. (a) Give IUPAC name of the compound represented by the structure :



P.T.O.

(b) The stability of carbocation follows the sequence :

(i) $3^\circ > 2^\circ > 1^\circ > \overset{+}{C}H_3$

(ii) $3^\circ > 2^\circ < 1^\circ < \overset{+}{C}H_3$

(iii) $3^\circ > 2^\circ > 1^\circ < \overset{+}{C}H_3$

(iv) $3^\circ < 2^\circ > 1^\circ < \overset{+}{C}H_3$.

(c) Write resonating structures of phenanthrene molecule.

(d) How many moles of styrene are contained in a polystyrene polymer whose molecular weight is 10^5 ?

(e) What are the alkaloids ? Why they are so called ? Give *one* example each of the following group of alkaloids :

(i) pyridine

(ii) isoquinoline

(iii) tropane.

(*f*) Which of the following pair hormones controls carbohydrate mechanism and of blood pressure ?

(*i*) Oxytocine and vasobrassin

(*ii*) Gastrin and secretin

(*iii*) Epinephrine and norepineprine

(*iv*) Cholecystokinin and pancreazymen.

(*g*) Which of the following groups of oils are rich in oleic acid/ester ?

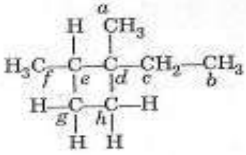
(*i*) Olive oil and palm oil

(*ii*) Kerosine oil and diesel oil

(*iii*) Clove oil and turpentine

(*iv*) Linseed oil and coconut oil.

(*h*) In the following representation of a hydrocarbon designate primary, secondary, tertiary and quaternary carbon atoms :



(*i*) How many chiral centres are there in glucose (aldohexose) molecule and how many pair of enantiomers of an aldohexose are known. Give the configurations of glucose and its epimer.

(*j*) Name the following :

(i) *two* compounds that are used as antiseptic

(ii) *one* antibiotic with four ring structures

(iii) *two* compounds that are used as analgesic

(iv) *one* compound that is used as antipyretic.

[Give chemical names in all cases except in case of antibiotic where other name is also permissible.] 10×3=30

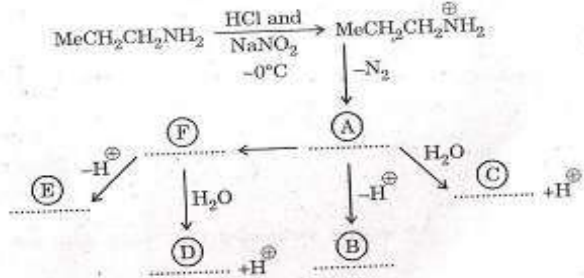
2. (a) (i) Explain the variation in base strength of the following compounds :

Compounds	NH_3,	$MeNH_2$,	Me_2NH,	Me_3N
pKb value	4.75	3.36	3.23	4.20

(ii) An organic compound picric acid does not have a carboxylic group yet it is strongly acidic (pKa = 1.03). Explain.

P.T.O.

(b) The mechanism of the reaction of *n*-propyl amine with nitrous acid is given below. Identify the organic compounds or organic species (ionic) A to F ignoring inorganic compounds and minor organic compounds if any :



[Me stands for methyl group, compounds B and E are same.]

(c) Write few lines what do you know about the following reaction intermediates :

(i) carbonium ion

(ii) carbanion

(iii) carbon radical

(iv) carbene.

(d) Complete the following chemical equations and identify these as electrophilic/nucleophilic addition, free radical reaction, nucleophilic/electrophilic substitution reaction. Also identify the organic compound/organic species A to F :

(i) $CH_3CH_2CH_2CH_2CHO + HCN$

$\longrightarrow$ (A) .....

(ii) $C_6H_6 \xrightarrow[\text{anhydrous } AlCl_3]{RCl}$ ..... (B) ..... (Friedel-Crafft alkylation reaction)

(iii) $C_6H_5\overset{\overset{O}{\|}}{C}-O-O-\overset{\overset{O}{\|}}{C}-C_6H_5 \longrightarrow$ ..... $\xrightarrow{2R^{\cdot}}$ (C), $R^{\cdot}$ = radical, identify it.

..... (C) $+ CH_2 = CH_2 \longrightarrow$ ..... (D)

..... (D) $+ nCH_2 = CH_2 \longrightarrow$ ..... (E)

..... (D) + ... (D) $\longrightarrow$ ..... (F)

(e) Complete the following chemical equations :

(i) electrophilic addition :

$CH_2 = CH-CH = CH_2 + HBr \xrightarrow{45^{\circ}}$ ..... (A) + ... (B)

(ii) rearrangement reaction :

$$CH_3—CH_2—CH_2 \cdot CH_3 \xrightarrow[\text{anhy. } AlCl_3]{\text{heat}} \underset{\text{(C)}}{\text{.....}}$$

$$CH_3—\underset{\underset{O}{\|}}{C}—\ddot{N}: \longrightarrow \underset{\text{(D)}}{\text{.....}}$$

(iii) elimination reaction :

$$CH_3CH_2OH \xrightarrow[170^\circ]{\text{concen. } H_2SO_4} \underset{\text{(E)}}{\text{.....}}$$

$$\begin{matrix} CH_2Br \\ | \\ CH_2Br \end{matrix} \xrightarrow[KOH]{\text{alcoholic}} \underset{\text{(F)}}{\text{.....}}$$

5×6=30

3. (a) Give the main organic products A to F ignoring minor organic and inorganic compounds if any :

(i) $CH_2\begin{matrix}\diagup COOEt \\ \diagdown COOEt\end{matrix} + C_6H_5CHO \xrightarrow[\text{piperidine}]{2^\circ\text{-amine}}$ $\underset{\text{(A)}}{\text{.....}}$, where Et = ethyl group

P.T.O.

(ii) $C_6H_5CHO + CH_3NO_2 \xrightarrow{KOH}$ ..... (B)

(iii) $CH_3COOC_2H_5 + CH_3COOC_2H_5$

$\xrightarrow[C_2H_5ONa]{EtOH}$ ..... (C)

$\downarrow H^+$

..... (D)

(iv) $CH_3COCH_3 + CH_3COCH_3 \xrightarrow[NaOH]{dilute}$ ..... (E)

(v) $C_6H_5COOEt + CH_3COOEt$

$\xrightarrow{C_2H_5ONa}$ ..... (F)

(Et stands for ethyl group)

(b) Give the main organic products A to F ignoring minor organic and inorganic products, if any :

(i) $CCl_3CHO \xrightarrow[heat]{Ca(OH)_2}$ ..... (A)

$\xrightarrow{HNO_3}$ ..... (B)

(ii) $H-C \equiv C-H + O_3 \longrightarrow$ ..... (C)

$\xrightarrow{H_2O}$ ..... (D)

(iii) $H-C \equiv C-H + NaOCl$

$\xrightarrow[\text{absence of light and air at } 0^\circ C]{\text{in}}$ ..... (E)

(iv) ..... (A) $\xrightarrow[KOH, \text{ warm}]{C_6H_5NH_2 \text{ and}}$ ..... (F)

(c) Give the main organic products A to F ignoring minor organic and inorganic products, if any :

(i) $BrCH_2COOEt + CH_3COCH_3 \xrightarrow[\text{ether}]{Zn}$

..... (A) $\xrightarrow{H_2O, H^+}$ ..... (B)

(ii) $CH_2(COOC_2H_5)_2 + NH_2CONH_2$

$\longrightarrow$ ..... (C)

(iii) $CH_3NH_2COOH \xrightarrow[\text{distill}]{Ba(OH)_2}$ ..... (D)

P.T.O.

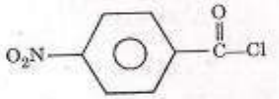
(iv) $C_{17}H_{31}COOH + H_2 \xrightarrow[\text{of Nickel}]{\text{in presence}}$ ..... (E)

(v) ..... (F) (Structure of natural rubber)

(d) Explain singlet and triplet states with schematic representation of electronic states in a molecule. Also explain energy transfer of singlet excitation and triplet excitation.

(e) Define Einstein's law of photochemical equivalence. What is quantum efficiency of a reaction ? Give the causes of low and high quantum yield. 5×6=30

4. (a) Give the main organic products A to F ignoring minor organic and inorganic products, if any :

(i) 

$$CH_3X \xrightarrow{Li} CH_3Li \xrightarrow{CuX} (CH_3)_2CuLi \xrightarrow{(CH_3)_2CuLi\ \text{i.e.,}}$$

..... (A)

(ii) $(CH_3)_3CHO + (CH_3)_3CHO \xrightarrow{NaOH}$

..... (B) + ... (C)

(iii) $\begin{matrix} C_2H_5 \\ CH_3 \end{matrix}\!\!>\!C = O + C_2H_5MgBr \longrightarrow$

$\xrightarrow[H_2O]{\text{hydrolysis}}$ ..... (D)

(iv) $CH_3CH_2CH_2CH_2MgBr + CO_2 \xrightarrow[\text{at low temp.}]{\text{pass } CO_2}$

$\xrightarrow[H_2O]{\text{hydrolysis}}$ ..... (E)

(v) $\begin{matrix} CH_2COOH \\ | \\ CH_2COOH \end{matrix} \xrightarrow{\text{bromination}} \begin{matrix} CHBrCOOH \\ | \\ CH_2COOH \end{matrix}$

$\xrightarrow[KOH]{\text{alcoholic}}$ ..... (F)

(give the name of F also)

(b) Give the main organic compounds A to F ignoring minor organic and inorganic products :

(i) $CH_2 = CH_2 + CH_2N_2 \longrightarrow$ ..... (A)

P.T.O.

(ii) $CH_3CH_2CH_2C(=O)Cl + CH_2N_2 \longrightarrow$ ..... (B) $\xrightarrow[H_2O]{\text{hydrolysis}}$ ..... (C)

(iii) $C_6H_5NHCH_3 + CH_2N_2 \longrightarrow$ ..... (D)

(iv) $CH_3CH = CHCH_3 + CH_2N_2 \longrightarrow$ ..... (E)

(v) $CH_3(CH_2)_{10}CH_2OH + 8$  $\xrightarrow{\text{base}}$ ..... (F)

Lauryl alcohol

(non-ionic detergent)

(c) Give the main organic compounds A to F ignoring minor organic and inorganic products, if any :

(i) $CH_3COCH_3 \xrightarrow[\text{passed over red hot platinum}]{\text{vapours}}$ ..... (A) $+ CH_4$

..... (C) $\xleftarrow{NH_3}$ (A) .....

(A) $\xrightarrow{\text{UV light}}$ ..... (B)

(ii) $CH_2(COOC_2H_5)_2 \xrightarrow{C_2H_5ONa} \xrightarrow{CH_3I}$

$\underset{(D)}{\text{.....}} \xrightarrow{C_2H_5ONa} \xrightarrow{C_2H_5I} \underset{(E)}{\text{.....}}$

$\xrightarrow[H_2O]{100^\circ C,\ NaOH}$

$\underset{(F)}{\text{.....}} \xleftarrow[150^\circ]{heat} CH_3CH_2C(CH_3)(COOH)_2$

(d) Give the main organic compounds A to F ignoring minor organic and inorganic products, if any :

(i) $CH_3CH_2CH_2CH_2CH_2CONH_2$

$\xrightarrow[\text{Hofmann Bromamide reaction}]{KOH,\ Br_2} \underset{(A)}{\text{.....}}$

(ii) $(CH_3)_2NH + HNO_2 \xrightarrow[HCl]{NaNO_2} \underset{(B)}{\text{.....}}$

P.T.O.

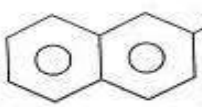
(iii) $CH_3COCH(CH_3)COOC_2H_5 \xrightarrow{\text{dilute NaOH}}$ ..... (C)

concen. ↓ alcoholic KOH

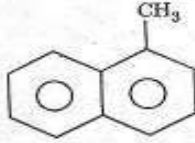
..... (D) + ... (E)

(iv) $C_6H_5MgCl + ClNH_2 \longrightarrow$ ..... (F)

(e) Give the main organic products A to F ignoring minor organic and inorganic products, if any. If no reaction takes write 'no reaction' with reason :

(i) $C_6H_5N = N—Cl +$ 

$\longrightarrow$ ..... (A)

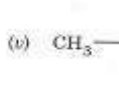
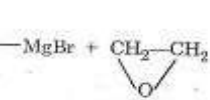
(ii) $C_6H_5N = N—Cl +$ 

$\longrightarrow$ ..... (B)

(iii)  +  $\xrightarrow{0°C}$ ..... (C)

$\xrightarrow{40°C}$ ..... (D)

(iv) $CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\underset{|}{\overset{|}{C}}}}-CH_2Cl + KCN \longrightarrow$ ..... (E)

(v)  + 

$\xrightarrow{\text{ether}}$ $\xrightarrow[H_2O]{\text{hydrolysis}}$ ..... (F)

5×6=30

5. (a) Which of the following oxidising agent is used to oxidise glucose to gluconic acid ? Give chemical equation. Why other remaining oxidising agents cannot be used for the purpose :

(i) ammonical solution of $AgNO_3$ (Tollen's reagent)

P.T.O.

(*ii*) alkaline solution of $CuSO_4$ in the presence of sodium citrate (Benedicts solution)

(*iii*) alkaline solution of $CuSO_4$ in the presence of sodium potassium tartrate (Rochelle's salt), (Fehling solution)

(*iv*) Bromine water

(*v*) Nitric acid.

(*b*) Aldehydes are more easily reduced than ketones. Give chemical equations for the following sequence of reactions by which an aldose (glucose) is converted into ketose (fructose) :

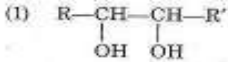
aldose ⟶ osazone ⟶ oson ⟶ ketose.

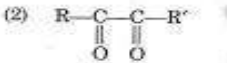
(*c*) Give the facts which could not be explained properly by Fischer's open chain structure for glucose. Write the proposed cyclic structure for glucose.

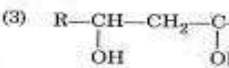
(d) (i) Give the properties which supports that sugar (cane sugar) does not contain free –CHO or  group.

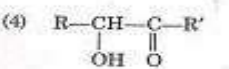
(ii) What is invert sugar ? How do you account for the experimentally observed $[\alpha] = -19.9$ for invert sugar ?

(e) (i) Which of the following compounds does not undergo oxidative cleavage of carbon-carbon bonds by periodic acid :

(1) 

(2) 

(3) 

(4) 

P.T.O.

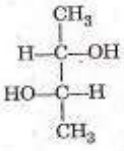
(ii) Whether glucose with HIO_4 undergoes oxidative cleavage or not. If yes, give chemical equation. 5×6=30

6. (a) Explain number-average molar mass $\overline{M_N}$ and mass average molar mass $\overline{M_M}$ in a polymer.

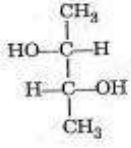
Equal number of molecules with M_1 = 10,000 and M_2 = 1,00,000 are mixed, calculate $\overline{M_N}$ and $\overline{M_M}$.

(b) 2, 3-dihydroxy butane has the structures I to IV :

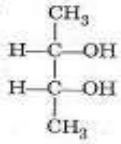
(I)



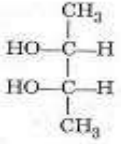
(II)



(III)



(IV)



Explain the following with identifications :

(1) number of chiral centres

(2) number of enantiomers

(3) number of diastereomers

(4) optical activity.

(c) (i) Write E, Z-configuration of 2-bromo-1-chloropropene.

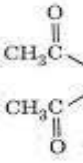
(ii) Distinguish between configurational isomer and confirmational isomer.

P.T.O.

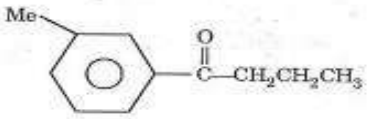
(iii) Give R, S-configuration for stereomers of 2, 3-dihydroxy butane [structure I to IV, question **6(b)**].

(d) Give the main organic compounds A to F ignoring inorganic and minor organic compounds, if any :

(i) $C_6H_5CHO + C_6H_5CHO \xrightarrow[KCN]{\text{alcoholic}}$ ..... (A)

(ii) $C_6H_5CHO +$  $\xrightarrow[CH_3COONa]{\text{in presence of}}$ ..... (B)

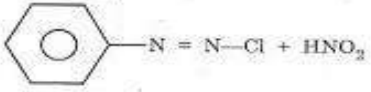
(iii) $C_6H_5-\underset{\underset{O}{\|}}{C}-(CH_2)_4-CH_3 \xrightarrow[\text{Climensen reduction}]{Zn \text{ and } HCl}$ ..... (C)

(iv) 

$$\xrightarrow[\text{NaOH}]{NH_2NH_2,} \quad \text{.....} \quad (D)$$

Wolf Kishner reduction

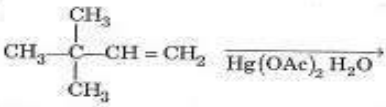
(v) $CH_3-\underset{\underset{CH_3}{|}}{C}=O + C_6H_5CHO \xrightarrow{NaOH}$ ..... (E)

(vi) 

$$\xrightarrow{Cu_2O} \quad \text{.....} \quad (F)$$

(c) Give the main organic compounds A to F ignoring minor organic and inorganic compounds. If no reaction takes place, write 'no reaction' :

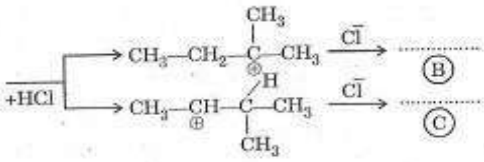
(i) oxymercuration-demercuration



$$\xrightarrow{Hg(OAc)_2\ H_2O} \xrightarrow{NaBH_4} \quad \text{.....} \quad (A)$$

P.T.O.

(ii) $CH_3-CH=\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-CH_3$



(iii) $\underset{\displaystyle CH(OH)COOH}{\overset{\displaystyle CH(OH)COOH}{\overset{|}{\underset{|}{}}}}$ $\xrightarrow{\text{heat}}$ ..... (D)

(iv) $ClCH_2COCl + H_2NCH_2COOH \longrightarrow$

..... (E) $\xrightarrow{NH_3}$ dipeptide ..... (F)

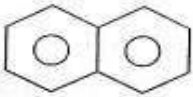
5×6=30

7. (a) (i) How many different mononitronaphthalene are possible ?

(ii) All carbon-carbon bonds in naphthalene are not the same. Explain.

(iii) From a theoretical stand point naphthalene has the structure required of an aromatic compound. Justify.

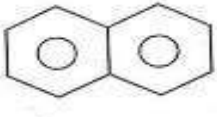
(b) Give the main organic compounds A to F ignoring minor organic compound and inorganic compound, if any :

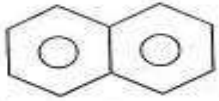
(i)  $\xrightarrow[\text{Na and reflux, } 132^\circ]{n\text{-pentyl alcohol,}}$

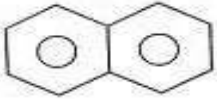
.....

(A)

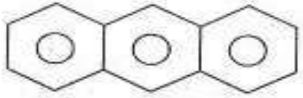
(ii)  $\xrightarrow[\text{anhy. } AlCl_3]{C_2H_5Br}$ ..... (B)

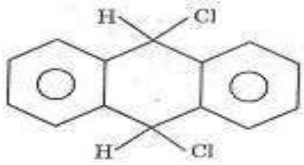
(iii)  $\xrightarrow[AlCl_3 \text{ (acylation)}]{C_6H_5NO_2,}$ ..... (C) + ... (D)

(iv)  $\xrightarrow[H_2SO_4 \text{ in presence of Hg, warm}]{\text{concen.}}$ ..... (E)

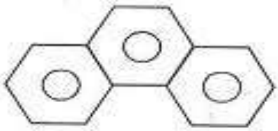
(v)  $\xrightarrow[CH_3COCl]{AlCl_3,\ C_2H_2Cl_4}$ ..... (F)

(c) Give the main organic compounds A to F ignoring minor organic and inorganic compounds, if any :

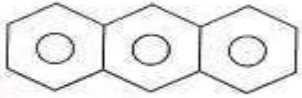
(i) 



..... (A)

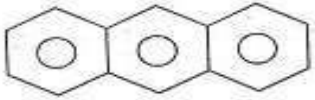
(ii) 

..... (B)

(iii) 

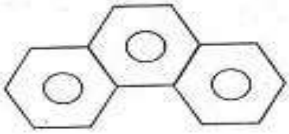
Saturated solution in C_6H_6, exposed to sun light ..... (C)

P.T.O.

(iv)  $\xrightarrow{HNO_3,\ excess}$

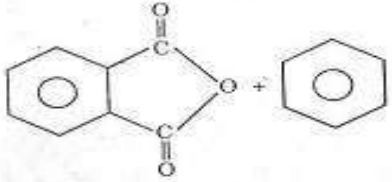
.....

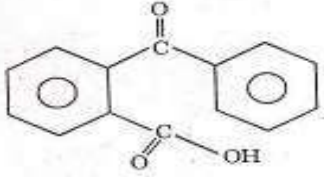
(D)

(v)  $\xrightarrow[H_2SO_4]{K_2Cr_2O_7,}$

.....

(E)

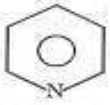
(vi)  $\xrightarrow{AlCl_3}$

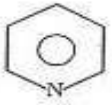
 $\xrightarrow[heat]{H_2SO_4}$

.....

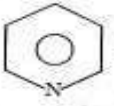
(F)

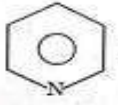
(d) Give the main organic compounds A to F ignoring minor organic and inorganic compounds, if any :

(i)  $\xrightarrow[\text{per benzoic acid}]{\text{oxidation}}$ ..... (A)

(ii)  $\xrightarrow[350°]{H_2SO_4}$ ..... (B)

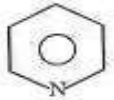
(iii)  $\xrightarrow[\text{of Nickel}]{H_2 \text{ in presence}}$ ..... (C)

(iv)  $\xrightarrow[HI]{\text{concen.}}$ ..... (D)

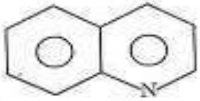
(v)  $\xrightarrow[\text{of by } NaNH_2 \text{ heat}]{\text{amination}} \xrightarrow{NH_3}$

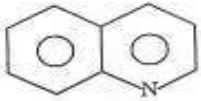
..... (E)

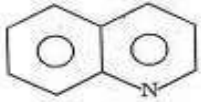
P.T.O.

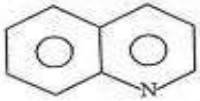
(vi)  + CH_3I ⟶ ..... (F)

(e) Give the main organic compounds A to F ignoring minor organic and inorganic compounds, if any :

(i)  + KOH $\xrightarrow{\text{heat}}$ ..... (A)

(ii)  $\xrightarrow{LiAlH_4}$ ..... (B)

(iii)  $\xrightarrow[300°]{Br_2}$ ..... (C)

(iv)  $\xrightarrow[\text{heat}]{\text{alkaline } KMnO_4}$ ..... (D)

$\xrightarrow{\text{heat}}$ ..... (E)

(v) $2C_2H_2 + HCN \xrightarrow[\text{HCN vapours in red hot tube}]{\text{pass } C_2H_2 \text{ and}}$ ..... (F)

5×6=30

8. (a) (1) Which of the following groups of two metals are present in all alloys given below :

German silver, delta metal, Brass, gun metal, bronze.

(i) Cu and Ni

(ii) Sn and Ni

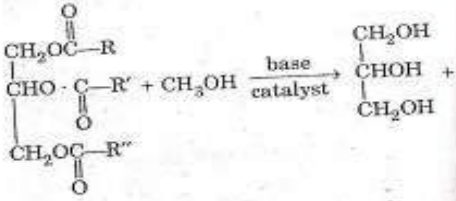
(iii) Sn and Zn

(iv) Cu and Zn.

(2) The compound alloy of Cu and Au crystallises

in a cubic lattice with copper at face centres and Au atoms at the corners. How many formula units of the compound are there in a unit cell.

(b) Give the main organic compounds A to F ignoring minor organic and inorganic compounds, if any :

(i) 

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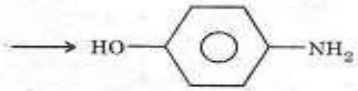
(ii) $C_6H_5CH = CHCOOH \xrightarrow[\text{reagent}]{\text{Baeyer's}}$ ..... (B)

(iii) $C_6H_5NO_2 \xrightarrow[\text{reduction in strongly acidic medium}]{\text{electrolytic}}$ ..... (C)



(iv) $C_6H_5NO_2 \xrightarrow[NH_4Cl]{\text{Zn dust,}}$ ..... (D)

(v) $C_6H_5NO_2 \xrightarrow[\text{Pt or Raney Ni (acid medium)}]{\text{hydrogenation}}$ ..... (E)

(vi) $C_6H_5NO_2 \xrightarrow[Pd]{LiAlH_4}$ ..... (F)

(c) Give the main organic compounds A to F ignoring minor organic and inorganic compounds, if any :

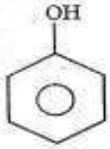
(i) $C_6H_5Cl + NH_3 \xrightarrow[60 \text{ atm. } 200^\circ C]{Cu_2Cl_2}$ ..... (A)

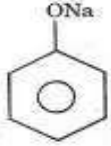
(ii) $C_6H_5CHO + C_6H_5NH_2 \xrightarrow{\text{heat}}$ ..... (B)

P.T.O.

(iii) $CH_3Li + N_2O \longrightarrow CH_2N = NOLi \longrightarrow$ ..... (C)

(iv) $C_6H_5NHNH_2 + CuO \xrightarrow[\text{solution}]{\text{Fehling}}$ ..... (D)

(v)  $\xrightarrow[0°C]{Br_2CS_2}$ ..... (E)

(vi)  $+ CO_2 \xrightarrow[125°]{\text{4-7 atm}}$ ..... (F)

(d) (i) Vitamins are small group of compounds, which of the following vitamin is a powerful antioxidant and its deficiency causes sterility particularly in animals :

(1) Vitamin K

(2) Vitamin B_2

(3) Vitamin E

(4) Vitamin C.

(ii) Give the main organic compounds A to C ignoring minor organic and inorganic compounds, if any :

(1) $CH_3CH(NH_2)COOH + HNO_2 \longrightarrow$ ..... (A)

(2) $H_2NCH_2CH_2COOH \xrightarrow{heat}$ ..... (B)

(3) $H_2NCH_2CH_2CH_2COOH \longrightarrow$ ..... (C)

(e) (i) All detergents have a common feature, a feature they share with ordinary soap, they are amphipathic. What is amphipathic ?

(ii) Name *three* essential fatty acids which of them is not available in our body but if made available in dietary fats, other two are made by the body itself.

(iii) Give the main organic compounds A and B ignoring minor organic and inorganic compounds, if any :

$$C_6H_5N = N—Cl + H_3PO_2 + H_2O \longrightarrow \text{.....}$$

(A)

$$C_6H_5N = N—Cl + HBF_4 \xrightarrow[\text{fluoboric acid}]{} C_6H_5\overset{+}{N}_2\overset{-}{B}F_4$$

$$\xrightarrow{\text{heat}} \text{.....}$$

(B)

5×6=30