PART : CHEMISTRY

1. For a weak monobasic acid a curve is drawn between $\frac{1}{\lambda_m}$ and $C\lambda_m$ where $\frac{1}{\lambda_m}$ is taken at y axis $C\lambda_m$ is taken at x axis.

If P is intercept at y axis & S is slope find ratio of $\frac{P}{S}$?

(λ_m^∞ = molar conductivity at ∞ dilution

λ_m^C = molar conductivity at concentration C

Ka = Ionisation constant of weak acid)

Ans. ($P/S = \lambda_m^\infty . Ka$)

Sol. $\alpha = \frac{\lambda_m}{\lambda_m^\infty}$ $\qquad$ $Ka = \frac{C\alpha^2}{1-\alpha}$

λ_m $1-\alpha$

$$Ka = C\left(\frac{\lambda_m}{\lambda_m^\infty}\right)^2 \Big/ \left(1-\frac{\lambda_m}{\lambda_m^\infty}\right)$$

$$= \frac{C\lambda_m^2}{\lambda_m^\infty\left(\lambda_m^\infty-\lambda_m\right)} = \frac{C\lambda_m}{\lambda_m^\infty\left(\frac{\lambda_m^\infty}{\lambda_m}-1\right)}$$

$$\frac{\lambda_m^\infty}{\lambda_m} - 1 = \frac{C\lambda_m}{\lambda_m^\infty.Ka}$$

$$\frac{\lambda_m^\infty}{\lambda_m} = 1 + \frac{C\lambda_m}{\lambda_m^\infty . Ka}$$

$$\frac{1}{\lambda_m} = \frac{1}{\lambda_m^\infty} + \frac{C\lambda_m}{(\lambda_m^\infty)^2 . Ka}$$

Intercept = $\frac{1}{\lambda_m^\infty}$ = P, Slope = S = $\frac{1}{(\lambda_m^\infty)^2 . Ka}$,

P/S = λ_m^∞ . Ka

2. Match the following :

	Reactions		Products
(I)	$P_2O_3 + H_2O \longrightarrow$	(P)	H_3PO_4
(II)	$P_4 + NaOH + H_2O \longrightarrow$	(Q)	$POCl_3$
(III)	$PCl_5 + CH_3COOH \longrightarrow$	(R)	PH_3
(IV)	$H_3PO_2 + H_2O + AgNO_3 \longrightarrow$	(S)	H_3PO_3

(A) (I) → (S) ; (II) → (R) ; (III) → (Q) ; (IV) → (P)
(B) (I) → (R) ; (II) → (S) ; (III) → (Q) ; (IV) → (P)
(C) (I) → (S) ; (II) → (R) ; (III) → (P) ; (IV) → (Q)
(D) (I) → (P) ; (II) → (R) ; (III) → (Q) ; (IV) → (S)

Ans. **(A)**

Sol. $P_2O_3 + H_2O \longrightarrow H_3PO_3$

$P_4 + NaOH + H_2O \longrightarrow PH_3 + NaH_2PO_2$

$PCl_5 + CH_3COOH \longrightarrow CH_3COCl + POCl_3 + HCl$

$H_3PO_2 + H_2O + AgNO_3 \longrightarrow H_3PO_4 + HNO_3 + Ag$

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3. Match the Column :

	Reactions		Products
(I)	$[Fe(H_2O)_6]^{+2}$	(P)	$t_{2g}^{1,1,1}\ e_g^{1,0}$
(II)	$[Co(H_2O)_6]^{+2}$	(Q)	$t_{2g}^{2,1,1}\ e_g^{1,1}$
(III)	$[FeCl_4]^-$	(R)	$t_{2g}^{2,2,1}\ e_g^{1,1}$
(IV)	$[Mn(H_2O)_6]^{+3}$	(S)	$t_{2g}^{1,1,1}\ e_g^{1,1}$

(A) (I) → (Q) ; (II) → (R) ; (III) → (S) ; (IV) → (P) (B) (I) → (R) ; (II) → (Q) ; (III) → (S) ; (IV) → (P)
(C) (I) → (Q) ; (II) → (S) ; (III) → (R) ; (IV) → (P) (D) (I) → (Q) ; (II) → (P) ; (III) → (R) ; (IV) → (S)

Ans. **(A)**

Sol. $[Mn(H_2O)_6]^{+3} \longrightarrow 3d^4$ + weak legand $t_{2g}^{1,1,1}\ e_g^{1,0}$

$[Fe(H_2O)_6]^{+2} \longrightarrow 3d^6$ + weak legand $t_{2g}^{2,1,1}\ e_g^{1,1}$

$[Co(H_2O)_6]^{+2} \longrightarrow 3d^7$ + weak legand $t_{2g}^{2,2,1}\ e_g^{1,1}$

$[FeCl_4]^- \longrightarrow 3d^5$ + weak legand $e_g^{1,1}\ t_{2g}^{1,1,1}$

4. Select the correct option(s)

(A) Calamine $\xrightarrow{\Delta}$ Zincite
(B) Impure Ag on treatment with NaCN in presence of O_2 forms a complex, which on reduction with Zn forms Ag
(C) Copperpyrite on heating with silica in reverberatory furnace to remove Fe impurity
(D) Malachite green on roasting forms cuprite

Ans. **(ABC)**

Sol. (A) $ZnCO_3 \xrightarrow{\Delta} ZnO + CO_2$

(B) $O_2 + H_2O + Ag + NaCN \longrightarrow Na[Ag(CN)_2]_{aq} + NaOH$

(C) $CuFeS_2 + O_2 \xrightarrow{\Delta} Cu_2S + FeO + SO_2$

$FeO + SiO_2 \longrightarrow FeSiO_2$

(D) $CuCO_3.Cu(OH)_2 \xrightarrow{\Delta} CuO + H_2O + CO_2$

5. Compressibility factor of a gas is 0.5 at 800K and X-atm. If it behaves as ideal gas at the given pressure and temperature its volume is Y. Find $\frac{X}{Y}$

Ans. **100**

Sol. $Z = \frac{PVm}{RT}$

$0.5 = \frac{X.0.4}{RT}$

$X \times 0.4 = 0.5\ RT$

$X \times 0.4 = 0.5\ R \times 800$

$X = R \times 1000$

$PVm = RT$

$R \times 1000 \times Y = R \times 800$

$Y = 0.8$

$\frac{X}{Y} = \frac{Rx1000}{0.8} = \frac{0.08x1000}{0.8}$

$\frac{X}{Y} = 100$

6. The complexes which can exhibit the type of isomerism as shown by $[Pt(NH_3)_2Br_2]$ is/are :
[en = $NH_2CH_2CH_2NH_2$]

(A) $[Zn(NH_3)_2Cl_2]$ (B) $[Cr(en)_2(H_2O)(SO_4)]^+$

(C) $[Pt(NH_3)_2Cl_4]$ (D) $[Pt(en)(SCN)_2]$

Ans. **(BC)**

Sol. $[Pt(NH_3)_2Br_2]$ exhibits cis-trans isomerism (Geometric isomerism)

(B) $[M(AA)_2ab]$ & $[Ma_2b_4]$ can exhibit geometric isomerism.

7. H_2S (5 mol) reacts completely with acidified aqueous $KMnO_4$ solution. In this reaction the number of moles of water produced is X, and the number of moles of electrons involved is Y. Determine the value of (X + Y).

Ans. **(18)**

Sol. $2KMnO_4 + 3H_2SO_4 + 5H_2S \longrightarrow K_2SO_4 + 2MnSO_4 + 8H_2O + 5S$

$X = 8$

$Y = 10$

8. For He+ ion a transition takes place from the orbit of radius 105.8 pm to the orbit of radius 26.45 pm. The wavelength (in nm) of the emitted photon during the transition is

Use, Bohr radius (a_0) = 52.9 pm

$R_H = 2.2 \times 10^{-18}J$

$h = 6.6 \times 10^{-34}$ J sec

$c = 3 \times 10^8$ m/sec

Ans. **(30 nm)**

Sol. $0.529 \times \frac{n_2^2}{2} = 1.058 \qquad n_2 = 2$

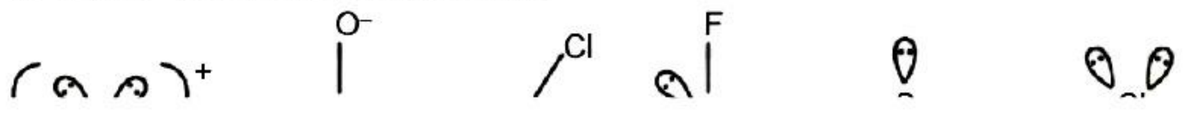
$0.529 \times \frac{n_1^2}{2} = .2645 \qquad n_1 = 1$

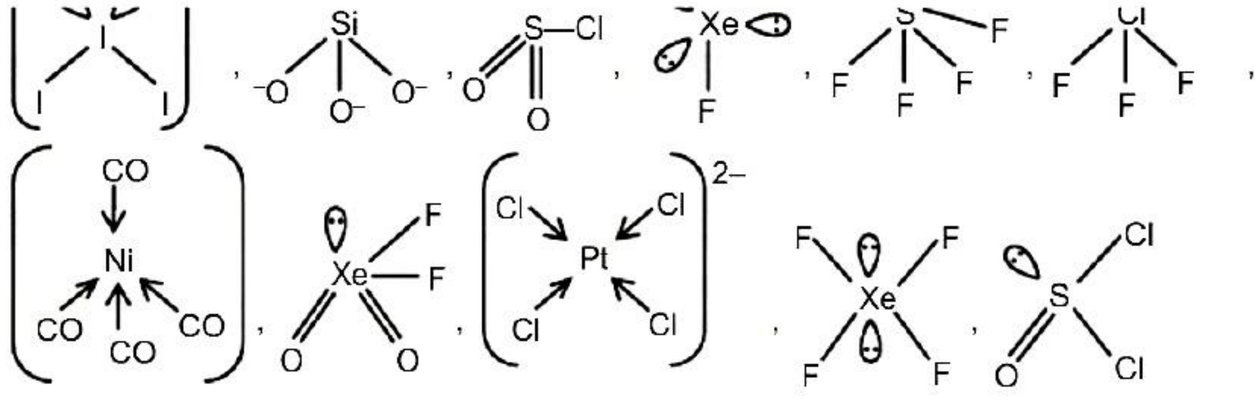
$\lambda = \frac{912}{2^2\left(\frac{1}{1^2} - \frac{1}{2^2}\right)} = 304\ Å = 30.4\ nm \approx 30\ nm$

9. Among $[I_3]^+$, $[SiO_4]^{-4}$, SO_2Cl_2, XeF_2, SF_4, Cl_3, $[Ni(CO)_4]$, XeO_2F_2, $[PtCl_4]^{2-}$, XeF_4, $SOCl_2$ the total number of species having sp^3 hybridized central atom.

Ans. **(5)**

$[I_3]^+$, $[SiO_4]^{-4}$, SO_2Cl_2, $[Ni(CO)_4]$, $SOCl_2$



Sol. 

10. 50 mL of 0.2 molal urea solution (density = 1.012 g ml^{-1} at 300 K) is mixed with 250 ml of a solution containing 0.06 g of urea. Both the solutions were prepared in the same solvent. The osmotic pressure (in torr) of the resulting solution M(urea) = 60 g mol^{-1} R = 62 L torr K^{-1} mol^{-1}

Assume $\Delta H_{mixing} = 0$ $\Delta V_{mixing} = 0$

Ans. **(682)**

Sol. 50 ml × 1.012 = 50.6 g = xg urea + (50.6 – x)g H_2O

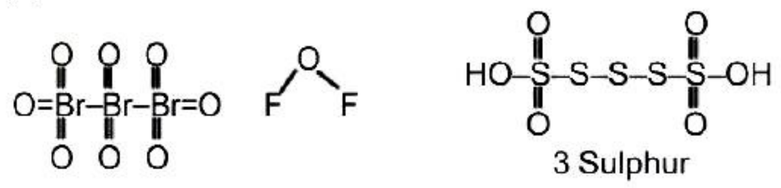
$$\text{molality} = 0.2 = \frac{\frac{x}{60}}{\frac{50.6-x}{1000}} \qquad x = 0.6 \text{ g urea} \equiv 0.01 \text{ mol urea}$$

Other solution has 0.06 g urea ≡ 0.001 mol urea

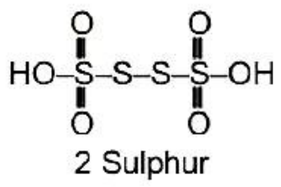
$$\pi_{resulting} = \frac{(0.01+0.001)}{0.3} \times 62 \times 300 = 682 \text{ torr}$$

11. Consider the following molecules Br_3O_8, OF_2, $H_2S_4O_6$, C_3O_2, and $H_2S_5O_6$. Count the number of atoms existing in their zero oxidation state in each molecule.

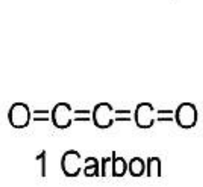
Ans. **(6)**

Sol. 

3 Sulphur



2 Sulphur



1 Carbon

12. For F_2 select the correct order of filling molecular orbitals:

(A) $\sigma 2p_z^2$, $\pi 2p_x^2 = \pi 2p_y^2$, $\pi^* 2p_x^2 = \pi^* 2p_y^2$

(B) $\pi 2p_x^2 = \pi 2p_y^2$, $\sigma 2p_z^2$, $\pi^* 2p_x^2 = \pi^* 2p_y^2$

(C) $\pi 2p_x^2 = \pi 2p_y^2$, $\pi^* 2p_x^2 = \pi^* 2p_y^2$, $\sigma 2p_z^2$

(D) $\pi^* 2p_x^2 = \pi^* 2p_y^2$, $\pi 2p_x^2 = \pi 2p_y^2$, $\sigma 2p_z^2$

Ans. **(A)**

Sol. Theory based

13. Atoms of metal x, y & z forms face centered cubic (fcc) unit cell of edge length L_x, Body centered unit cell (bcc) unit cell of edge length L_y and simple cubical unit cell (SC) of edge length L_z respectively

It $r_z = \frac{\sqrt{3}}{2} r_y$, $r_y = \frac{8}{\sqrt{3}} r_x$

$M_z = \frac{3}{2} M_y$, $M_z = 3M_x$

Given M_x, M_y, M_z are molar mass of metal x, y & z.

r_x, r_y, r_z are atomic radii of x, y & z

Identify the correct statement(s)

(A) Packing efficiency x > y > z

(B) Density of x > Density of y

(C) $L_x > L_y$

(D) $L_y > L_z$

Ans. **(AB)**

Ans. (AD)

Sol. Packing efficiency

FCC $\quad PE = \dfrac{4\times 4/3\pi r_x^3}{(L_x)^3} = \dfrac{4\times 4/3\pi r_x^3}{\left(\dfrac{4rx}{\sqrt{2}}\right)^3}$

BCC $\quad PE = \dfrac{2\times 4/3\pi r_y^3}{(L_y)^3} = \dfrac{2\times 4/3\pi r_y^3}{\left(\dfrac{4r_y}{\sqrt{3}}\right)^3}$

S.C. $\quad PE = \dfrac{1\times 4/3\pi r_z^3}{(L_z)^3} = \dfrac{1\times 4/3\pi r_z^3}{(2r_z)^3}$

PE $\quad$ FCC : BCC : SC

$= \dfrac{4\times(\sqrt{2})^3}{(4)^3} : \dfrac{4\times(\sqrt{3})^3}{(4)^3} : \dfrac{1}{(2)^3}$

$= \dfrac{2\sqrt{2}}{16} : \dfrac{2\times 3\times\sqrt{3}}{16} : \dfrac{1}{8}$

$= 8\sqrt{2} : 6\sqrt{3} : 8$

$= 11.3 : 10.392 : 8$

$L_x = \dfrac{4r_x}{\sqrt{2}}$, $L_y = \dfrac{4r_y}{\sqrt{3}}$, $L_z = 2r_z$

$L_x < L_y$

$\dfrac{L_x}{L_y} = \dfrac{r_x}{r_y}\cdot\dfrac{\sqrt{3}}{\sqrt{2}} = \dfrac{\sqrt{3}}{8}\times\dfrac{\sqrt{3}}{\sqrt{2}} = \dfrac{3}{8\sqrt{2}}$

$L_y = \dfrac{4r_y}{\sqrt{3}}$, $L_z = 2r_z$

$\dfrac{L_y}{L_z} = \dfrac{2r_y}{r_z.\sqrt{3}} = \dfrac{2}{\sqrt{3}}\times\dfrac{\sqrt{3}}{2} = \dfrac{1}{1}$

$(\text{Density})_\alpha = \dfrac{4M_x}{N_A(L_x)^3}$, $(\text{Density})_y = \dfrac{2M_y}{N_A(L_y)^3}$

$\dfrac{d_x}{d_y} = \dfrac{2M_x}{M_y}\cdot\left(\dfrac{L_y}{L_x}\right)^3$

$= 2\times\dfrac{1}{2}\times\left(\dfrac{8\sqrt{2}}{3}\right)^3$

SO: $d_x > d_y$

14. $(P)\xrightarrow{NaOH}\underset{\text{white ppt}}{(Q)} + (R)$

$(Q)\xrightarrow{PbO_2\,\&\,H^-}\underset{\text{Pink coloured solution}}{(S)}$

$(R)\xrightarrow{MnO(OH)_2}(T)$

which produce blue dots on starch iodide paper (S) & (T) are respectively:

(A) $KMnO_4$, Cl_2 (B) K_2MnO_4, HCl (C) MnO_2, ClO_3^- (D) K_2MnO_4, ClO_2^-

Ans. **(A)**

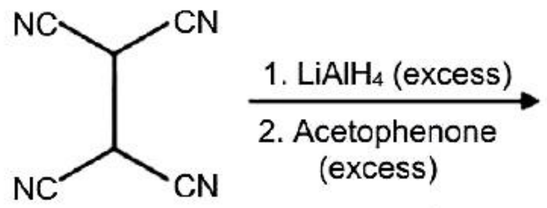
Sol. $Mn^{+2}_{(P)} \xrightarrow{NaOH} \underset{(Q)\text{ white ppt}}{Mn(OH)_2\downarrow}$

$PbO_2 + Mn^{+2} + H^+ \longrightarrow \underset{(S)}{MnO_4^-} + Pb^{+2} + H_2O$

$Cl^- + MnO(OH)_2 \longrightarrow \underset{(T)}{Cl_2}$

which gives starch iodide test.

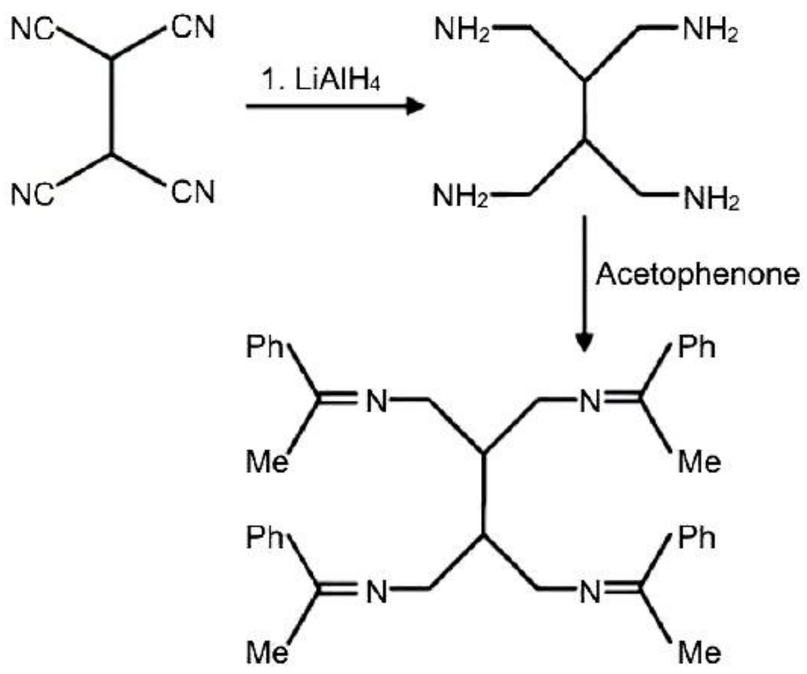
15.



Heterocyclic compound is not formed in final product then total number of sp^2 carbon atoms in the final product is

Ans. **28**

Sol.



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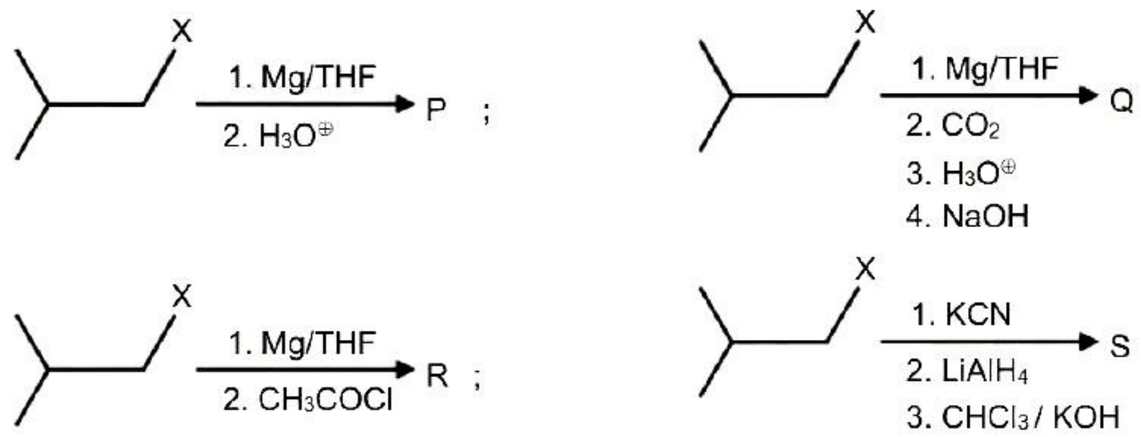


Which of the following is correct for above given reactions

(A) Q give Kolbe's electrolytic synthesis and its product has eight carbon atoms

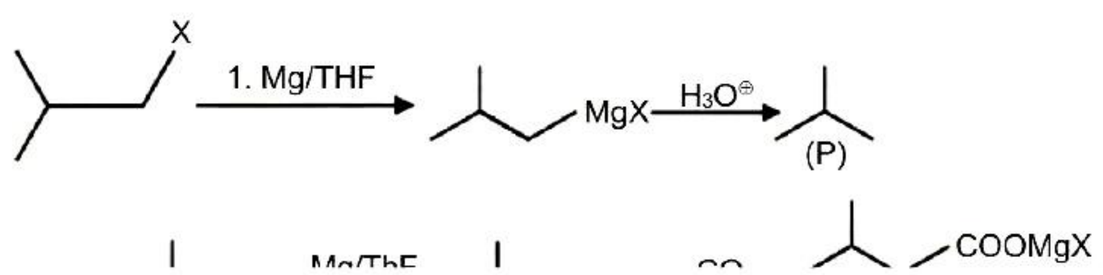
(B) S is a primary amine

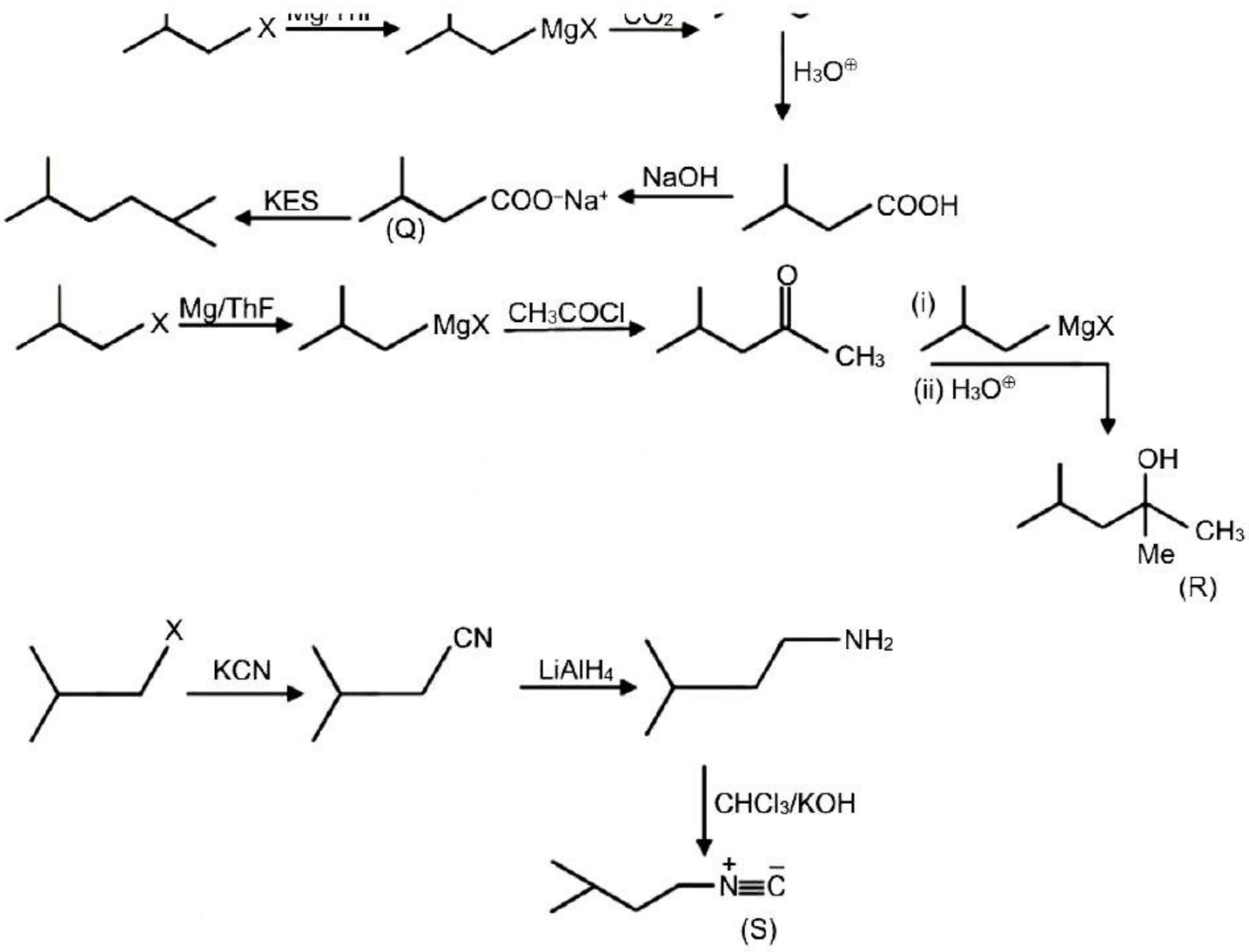
(C) R gives Cannizaro's reaction

(D) P is a primary alcohol

Ans. **(A)**

Sol.





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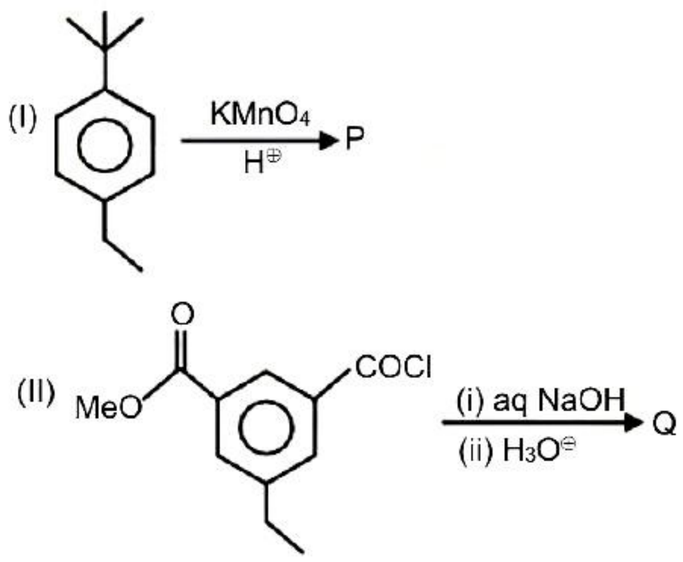
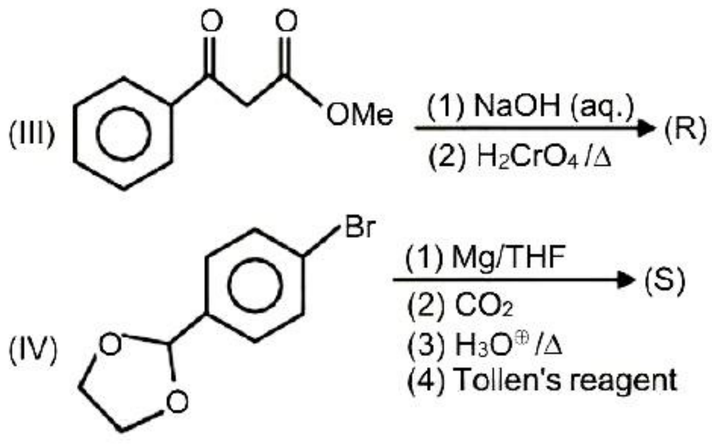




Which of the following is/are correct

(A) Compound P and Q can be monomer of Dacron & Glyptal respectively

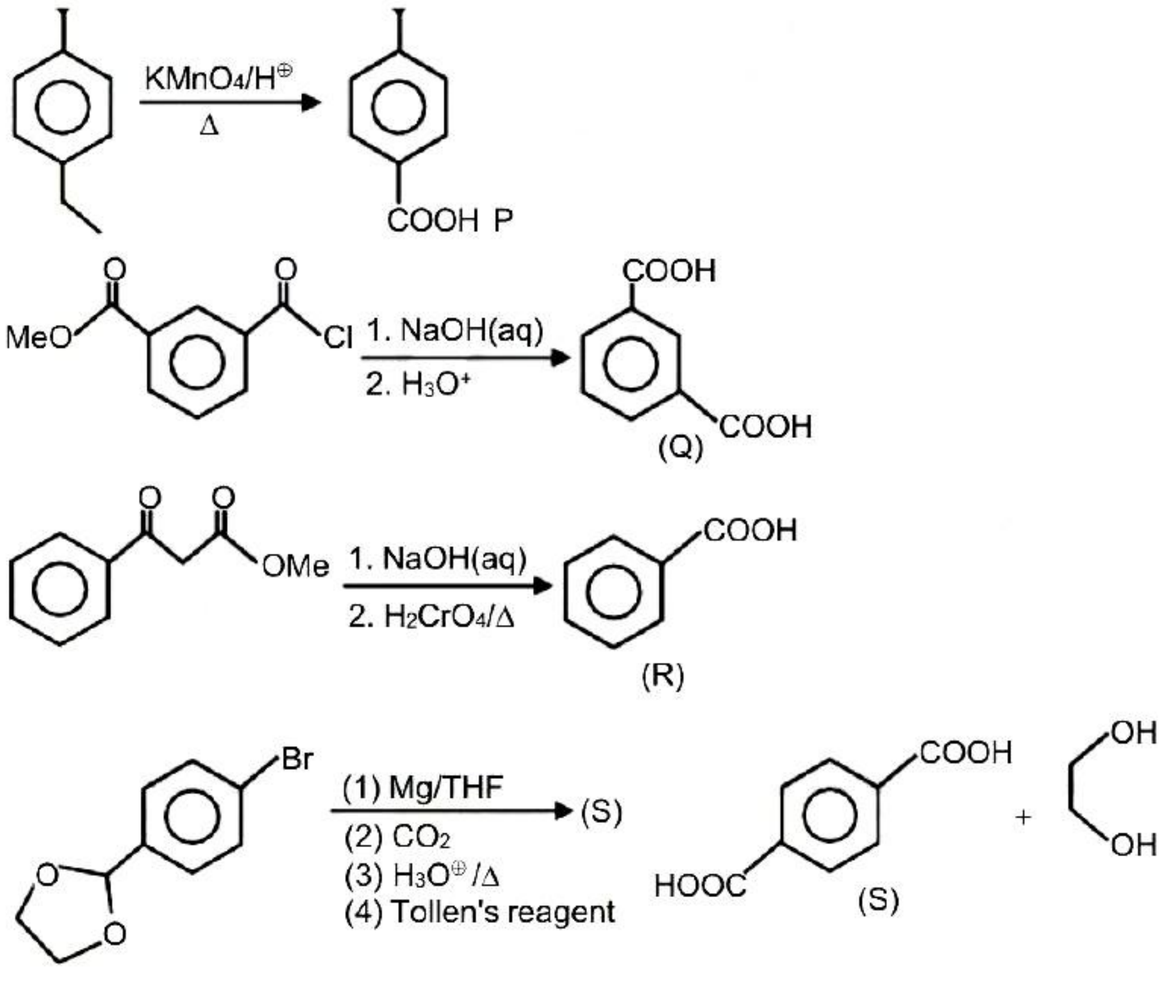
(B) Q & S are Dicarboxylic acids

(C) Q & R are same compound

(D) P, Q & R are structural isomers

Ans. **(B)**

Sol.



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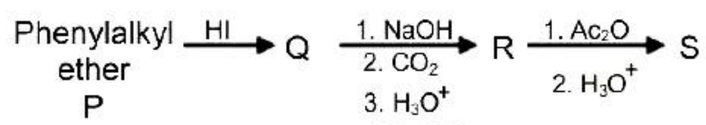
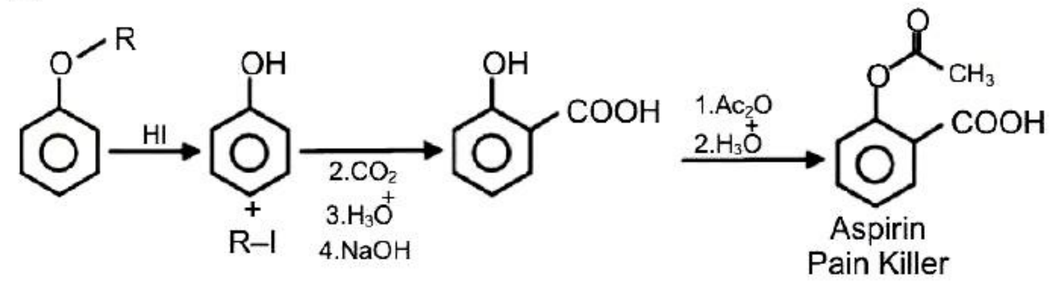


Compound S is ?

(1) O–Acetoxy benzoic acid
(2) It inhibits prostaglandins
(3) It is a narcotic analgesic
(4) It inhibits the enzyme which degrades noradrenaline

Ans. **(1)**

Sol.

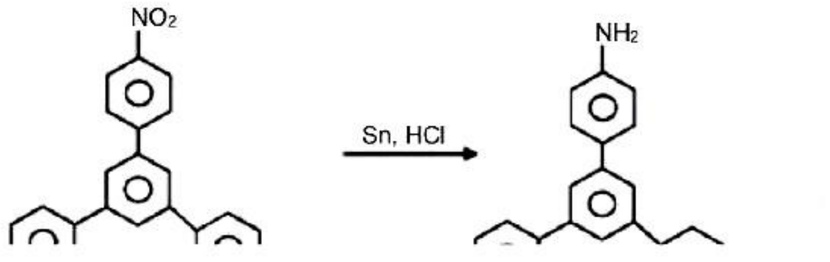


Paragraph/Comprehension

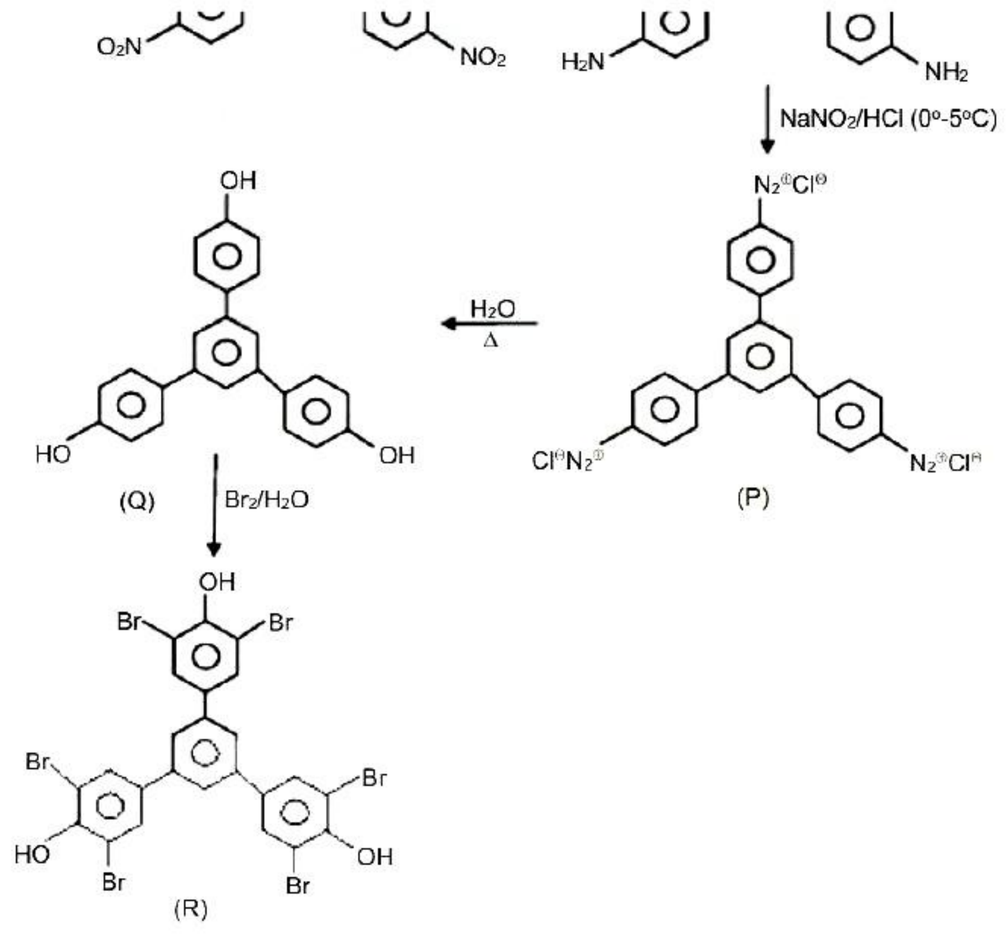
1,3,5 Tris (4-nitrophenyl) benzene is reacted with Sn/HCl, product is further reacted to $NaNO_2$ and HCl at 0°-5°C tempreture that gives product 'P', product 'P' is heated with water at room temp. gives compound Q, Q is brominated in aqueous medium, now compound 'P' is reacted with excess of Phenol in basic medium giving 'S' molar mass difference of compound Q and R is 474.

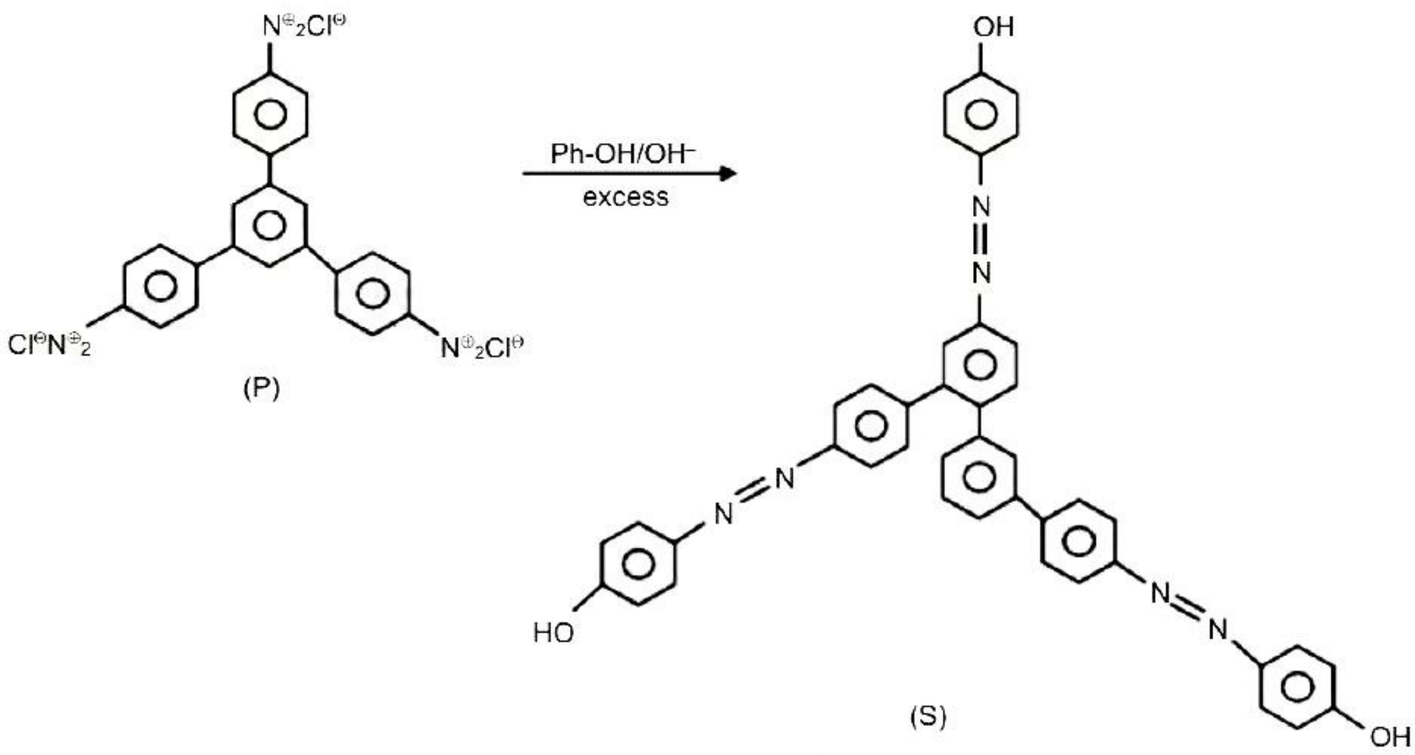
19. Number of heteroatom in R is

Ans. **9**



Sol.

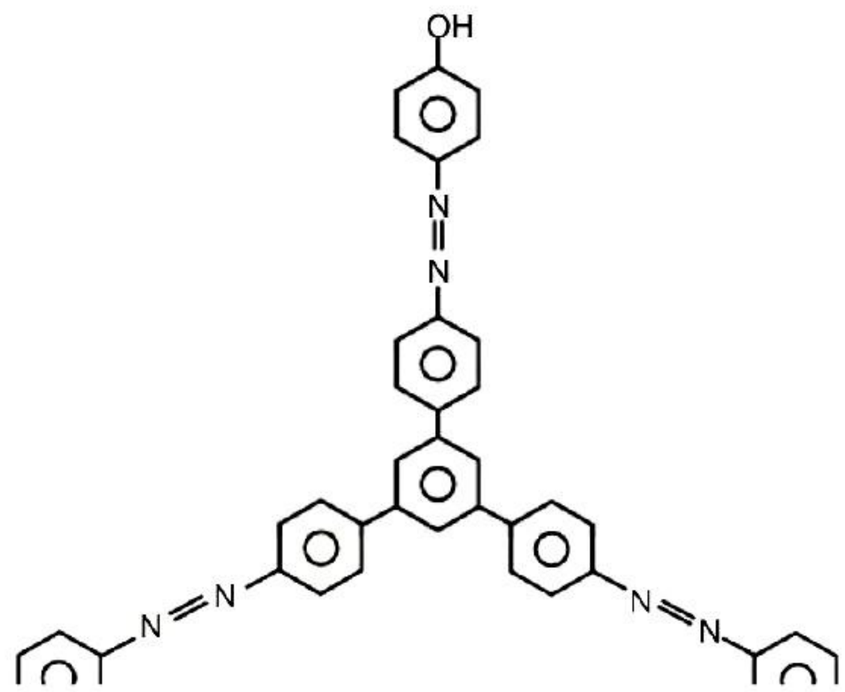


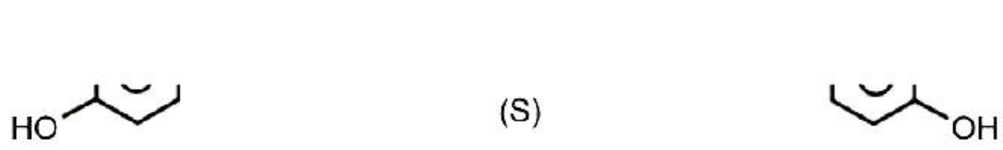


20. If molar mass difference of S and P is 172.5 then sum of total carbon and hetroatoms in product 'S' is :

Ans. **51**

Sol.




HO
(S)
OH