JEE (ADVANCED) 2018

CHEMISTRY (PAPER 1)

SECTION 1

- This section contains **SIX (06)** questions.
- Each question has **FOUR** options for correct answer(s). **ONE OR MORE THAN ONE** of these four option(s) is (are) correct option(s).

1. The compound(s) which generate(s) N_2 gas upon thermal decomposition below 300°C is (are)

(A) NH_4NO_3

(B) $(NH_4)_2Cr_2O_7$

(C) $Ba(N_3)_2$

(D) Mg_3N_2

Solution

(B), (C) Ammonium salts decompose quite readily on heating. If the anion is more oxidizing (e.g. $NO_3^-, Cr_2O_7^{2-}$) then NH_4^+ is oxidized to N_2 or N_2O.

$$NH_4NO_3 \xrightarrow{\text{Heat}} N_2O + 2H_2O$$
$$(NH_4)_2Cr_2O_7 \xrightarrow{\text{Heat}} N_2 + 4H_2O + Cr_2O_3$$
$$Ba(N_3)_2 \xrightarrow{\text{Heat}} Ba + N_2$$

Mg_3N_2 is an ionic compound, therefore, will not decompose at 300°C.

2. The correct statement(s) regarding the binary transition metal carbonyl compounds is (are) (Atomic numbers: Fe = 26, Ni = 28)

(A) Total number of valence shell electrons at metal centre in $Fe(CO)_5$ or $Ni(CO)_4$ is 16.

(B) These are predominantly low spin in nature.

(C) Metal–carbon bond strengthens when the oxidation state of the metal is lowered.

(D) The carbonyl C–O bond weakens when the oxidation state of the metal is increased.

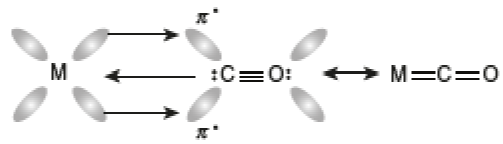
Solution

(B), (C) Option (A): Incorrect. Total number of valence shell electrons in $Fe(CO)_5$ [8 + 5× 2 = 18] and $Ni(CO)_4$ [10 + 4× 2 = 18] is 18.

Option (B): **C**orrect. CO being a strong field ligand cause pairing of electrons.

Hence, both the complexes formed are low spin in nature.

Option (C): Correct. CO ligand not only donates the lone pair of electrons to the central atom but also accept the electron cloud from the central atom in their low-lying vacant orbitals. This kind of back donation is known as 'synergic effect' or 'synergic bonding. In case of CO, the back donation to the π* orbital of central atom may be depicted as:



Greater the electron density on the metal atom, that is, lower the oxidation state of the metal, greater will be the back donation hence stronger will be the M–C bond.

Option (D): Incorrect. When the oxidation state of metal increases its tendency to accept the electrons from C of CO increases but the acceptance of electrons of CO from central atom decreases consequently M–C bond strength decreases and C–O bond strength increases.

3. Based on the compounds of group 15 elements, the correct statement(s) is (are)

(A) Bi_2O_5 is more basic than N_2O_5.

(B) NF_3 is more covalent than BiF_3.

(C) PH_3 boils at lower temperature than NH_3.

(D) The N–N single bond is stronger than the P–P single bond.

Solution

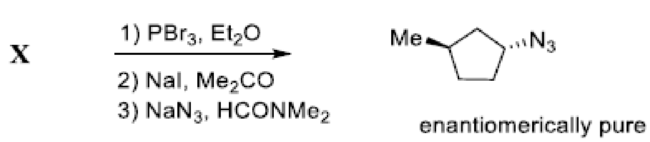
(A), (B), (C) Option (A): Correct. The basicity of oxides usually increases on descending a group. Therefore, Bi_2O_5 is more basic than N_2O_5.

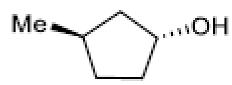
Option (B): Correct. Covalent nature of a molecule depends on the electronegativity difference between bonded atoms.

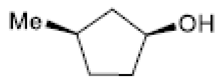
Option (C): Correct. Boiling point of NH_3 is more than that of PH_3 due to hydrogen bonding.

Option (D): Incorrect. P–P single bond is stronger than N–N single bond. This is due to the fact that N is small in size, due to smaller size of atoms lone pair of repulsion will be more.

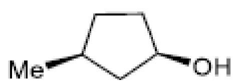
4. In the following reaction sequence, the correct structure(s) of **X** is (are)



(A) 

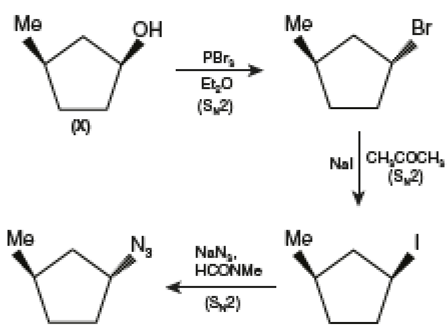
(B) 

(C) 

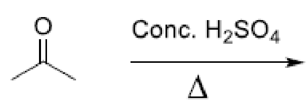
(D) 

Solution

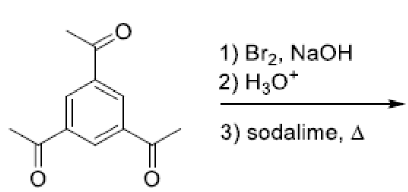
(B)

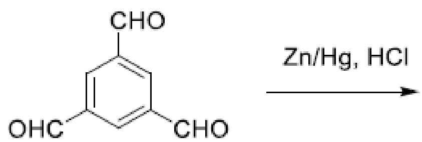


5. The reaction(s) leading to the formation of 1, 3, 5-trimethylbenzene is (are)

(A) 

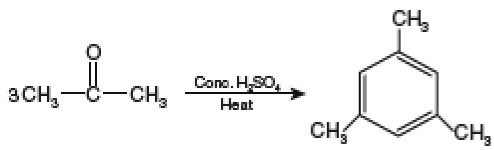
(B) 

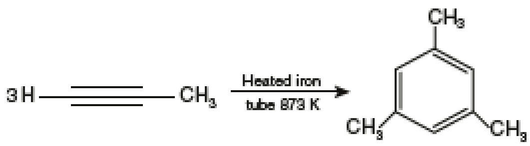
(C) 

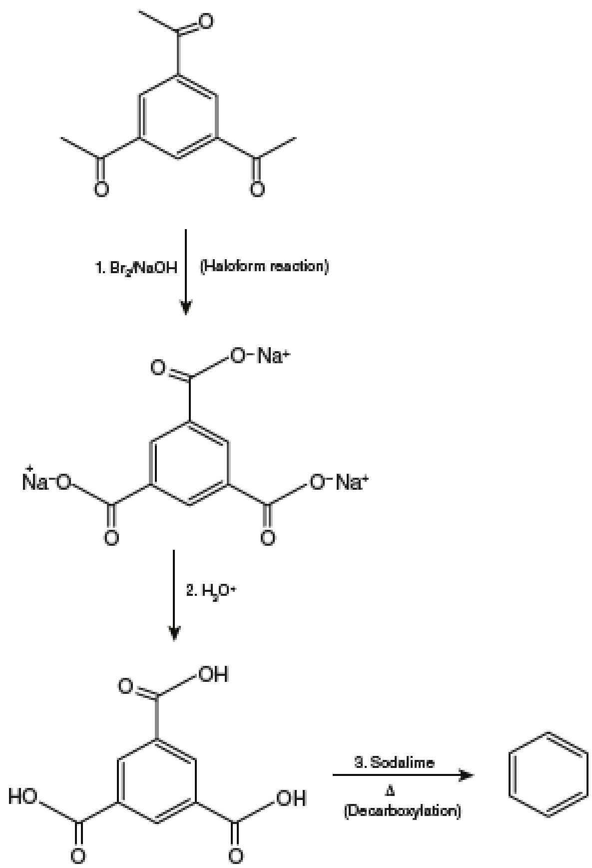
(D) 

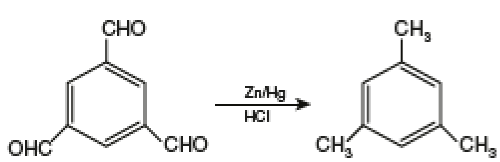
Solution

(A), (B), (D)

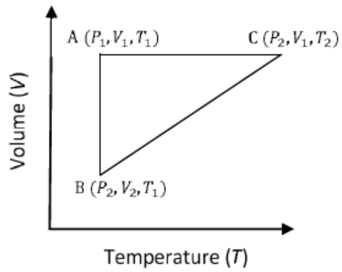








6. A reversible cyclic process for an ideal gas is shown below. Here, P, V, and T are pressure, volume and temperature, respectively. The thermodynamic parameters q, w, H and U are heat, work, enthalpy and internal energy, respectively.



The correct option(s) is (are)

(A) $q_{AC} = \Delta U_{BC}$ and $w_{AB} = P_2(V_2 - V_1)$

(B) $w_{BC} = P_2(V_2 - V_1)$ and $q_{BC} = \Delta H_{AC}$

(C) $\Delta H_{CA} < \Delta U_{CA}$ and $q_{AC} = \Delta U_{BC}$

(D) $q_{BC} = \Delta H_{AC}$ and $\Delta H_{CA} > \Delta U_{CA}$

Solution

(B), (C) We know $\Delta U = q + w$ and $w = -P\Delta V$

For an isochoric process AC as $\Delta V = 0$, therefore, $w_{AC} = 0$ and $\Delta U_{AC} = q$

For an isobaric process BC, we have $\Delta U_{BC} = q_{BC} + w_{BC}$

$$w_{BC} = -P_2(V_1 - V_2) = P_2(V_2 - V_1)$$

$$\Delta H_{BC} = q_{BC}$$

Since, $(\Delta T)_{AC} = (\Delta T)_{BC}$

Therefore, $\Delta U_{BC} = \Delta U_{AC} = q_{AC}$

$$\Delta H_{BC} = \Delta H_{AC} = q_{BC}$$

Since, $T_2 > T_1$

ΔH_{CA} and ΔU_{CA} are negative.

$$\Delta H_{CA} = \Delta U_{CA} + V\Delta P$$

As $\Delta P < 0$, therefore, $\Delta H_{CA} < \Delta U_{CA}$.

SECTION 2

- This section contains **EIGHT (08)** questions. The answer to each question is a **NUMERICAL VALUE**.
- For each question, enter the correct numerical value (in decimal notation, truncated/rounded-off to the **second decimal place**; e.g. 6.25, 7.00, –0.33, –.30, 30.27, –127.30) using the mouse and the on-screen virtual numeric keypad in the place designated to enter the answer.
- Answer to each question will be evaluated according to the following marking scheme:

7. Among the species given below, the total number of diamagnetic species is ___.

H atom, NO_2 monomer, O_2^- (superoxide), dimeric sulphur in vapor phase,

Mn_3O_4, $(NH_4)_2[FeCl_4]$, $(NH_4)_2[NiCl_4]$, K_2MnO_4, K_2CrO_4

Solution

(1) The paramagnetic species are H atom, NO_2 monomer, O_2^- (superoxide), dimeric sulphur in vapor phase, Mn_3O_4, $(NH_4)_2[FeCl_4]$, $(NH_4)_2[NiCl_4]$ and K_2MnO_4.

The diamagnetic species is K_2CrO_4.

8. The ammonia prepared by treating ammonium sulphate with calcium hydroxide is completely used by $NiCl_2 \cdot 6H_2O$ to form a stable coordination compound. Assume that both the reactions are 100% complete. If 1584 g of ammonium sulphate and 952 g of $NiCl_2 \cdot 6H_2O$ are used in the preparation, the combined weight (in grams) of gypsum and the nickel–ammonia coordination compound thus produced is_____.

(Atomic weights in g mol^{-1}: H = 1, N = 14, O = 16, S = 32, Cl = 35.5, Ca = 40, Ni = 59)

Solution

$$\underset{\substack{132\text{ g} = 1\text{ mol} \\ 1584\text{ g} = 12\text{ mol}}}{(NH_4)_2SO_4} + Ca(OH)_2 \rightarrow \underset{12\text{ mol}}{CaSO_4 \cdot 2H_2O} + \underset{24\text{ mol}}{2NH_3}$$

$$\underset{\substack{238\text{ g} = 1\text{ mol} \\ 952\text{ g} = 4\text{ mol}}}{NiCl_2 \cdot 6H_2O} + \underset{24\text{ mol}}{6NH_3} \rightarrow \underset{4\text{ mol}}{[Ni(NH_3)_6]Cl_2} + 6H_2O$$

So, total mass of products is

$$12 \times 172 \text{ (gypsum)} + 4 \times 232 \text{ ([Ni(NH}_3)_6]\text{Cl}_2) = 2992 \text{ g}$$

9. Consider an ionic solid **MX** with NaCl structure. Construct a new structure (**Z**) whose unit cell is constructed from the unit cell of **MX** following the sequential instructions given below. Neglect the charge balance.

(i) Remove all the anions (**X**) except the central one

(ii) Replace all the face centered cations (**M**) by anions (**X**)

(iii) Remove all the corner cations (**M**)

(iv) Replace the central anion (**X**) with cation (**M**)

The value of $\left(\frac{\text{number of anions}}{\text{number of cations}}\right)$ in ***Z*** is ______.

Solution

(3) Given that MX is an ionic solid having NaCl type structure having ccp. So, the anion X^- occupies all octahedral voids. The changes (i)-(iv) cause the following effects:

(i) No. of anions left = 1

(ii) No. of anions added by replacing face centered cations M = 3; No. of cations left = 1

(iii) No. of cations left = 0

(iv) No. of cations added = 1; No. of anions left = 3

Finally, the unit cell contains 1 cation and 3 anions. So,

The value of $\left(\frac{\text{number of anions}}{\text{number of cations}}\right)$ in ***Z*** is 3.

10. For the electrochemical cell,

$$Mg(s)\,|\,Mg^{2+}\,(aq,\,1\,M)\,||\,Cu^{2+}\,(aq,\,1\,M)\,|\,Cu(s)$$

the standard emf of the cell is 2.70 V at 300 K. When the concentration of Mg^{2+} is changed to x M, the cell potential changes to 2.67 V at 300 K. The value of ***x*** is_______.

(Given, $\frac{F}{R}$ = 11500 K V^{-1}, where F is the Faraday constant and R is the gas constant, ln(10) = 2.30)

Solution

(10) The cell reaction is

$$\text{Mg(s)} + \text{Cu}^{2+}(\text{aq, 1 M}) \rightarrow \text{Mg}^{2+}(\text{aq, } x \text{ M}) + \text{Cu(s)}$$

$$E_{cell} = E^{o}_{cell} - 2.303 \times \frac{RT}{2F} \log \frac{[Mg^{2+}]}{[Cu^{2+}]}$$

$$2.67 = 2.70 - 2.303 \times \frac{300}{2 \times 11500} \log(x)$$

$$0.03 = \frac{2.303 \times 3}{115 \times 2} \log x \Rightarrow \log x = 1 \Rightarrow x = 10$$

11. A closed tank has two compartments **A** and **B**, both filled with oxygen (assumed to be ideal gas). The partition separating the two compartments is fixed and is a perfect heat insulator (Figure 1). If the old partition is replaced by a new partition which can slide and conduct heat but does **NOT** allow the gas to leak across (Figure 2), the volume (in m^3) of the compartment **A** after the system attains equilibrium is_.

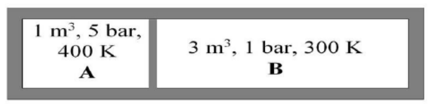


Figure 1

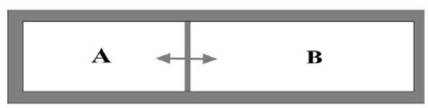


Figure 2

Solution

(2.22) Using $pV = nRT$, we have

In Figure 1,

$$n_A = \frac{p_A V_A}{RT} = \frac{5}{400R} \text{ and } n_B = \frac{p_B V_B}{RT} = \frac{1}{100R}$$

In Figure 2, after equilibrium is attained, we have

$$p_A = p_B \text{ and } T_A = T_B = T, \text{ so}$$

$$\frac{n_A RT}{V_A} = \frac{n_B RT}{V_B} \Rightarrow \frac{5}{400R \cdot V_A} = \frac{1}{100R \cdot V_B}$$

$$\Rightarrow 4V_A = 5V_B$$

Now, $V_A + V_B = 4 \text{ m}^3$, so $V_A + \frac{4}{5}V_A = 4 \Rightarrow V_A = \frac{20}{9} = 2.22 \text{ m}^3$

12. Liquids **A** and **B** form ideal solution over the entire range of composition. At temperature T, equimolar binary solution of liquids **A** and **B** has vapor pressure 45 torr. At the same temperature, a new solution of **A** and **B** having mole fractions x_A and x_B, respectively, has vapor pressure of 22.5 torr. The value of x_A/x_B in the new solution is

(Given that the vapor pressure of pure liquid **A** is 20 torr at temperature T)

Solution

$$p_A^o x_A + p_B^o x_B = p_T = 45$$

For equimolar binary solution, $x_A = x_B = 0.5$, so

$$20 \times 0.5 + p_B \times 0.5 = 45 \Rightarrow 70 \text{ torr}$$

For the new solution,

$$p_B^o + (p_A^o - p_B^o)x_A = 22.5 \Rightarrow 70 + (20-70)x_A = 22.5 \Rightarrow x_A = 47.5/50$$

Now, $$\frac{x_A}{x_B} = \frac{x_A}{1-x_A} = \frac{47.5/50}{1-(47.5/50)} = \frac{47.5}{2.5} = 19$$

13. The solubility of a salt of weak acid (**AB**) at pH 3 is **Y** × 10^{-3} mol L^{-1}. The value of **Y** is_______.

(Given that the value of solubility product of **AB** (K_{sp}) = 2×10^{-10} and the value of ionization constant of **HB** (K_a) = 1×10^{-8})

Solution

The reactions are

$$\underset{}{AB(s)} \rightleftharpoons \underset{S}{A^+(aq)} + \underset{S-x}{B^-(aq)}$$

$$\underset{S-x}{B^-(aq)} + \underset{10^{-3}}{H^+(aq)} \rightleftharpoons HB$$

Now, for HB,

$$K_a = \frac{[H^+][B^-]}{[HB]} \Rightarrow \frac{(s-x)\times 10^{-3}}{x} = 10^{-8}$$

$$\Rightarrow s - x = x \times 10^{-5}$$

$$K_{sp} = [A^+][B^-] = S(S-x) = 2 \times 10^{-10}$$

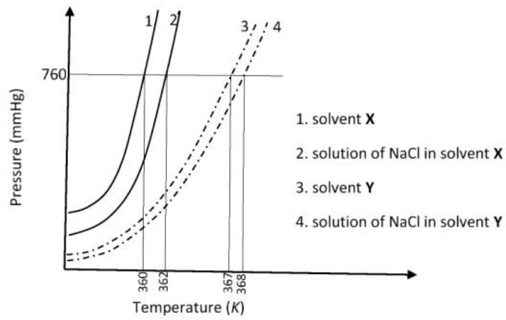
Putting $Sx = 2 \times 10^{-5}$ in $S^2 - Sx - 2\times 10^{-10} = 0$, we get

$$S \approx \sqrt{(2\times 10^{-5})} = 4.47 \times 10^{-3} \text{ M}$$

Alternate solution

$$S = \sqrt{K_{sp}\left(\frac{[H^+]}{K_a} + 1\right)} = \sqrt{20 \times 10^{-10}\left(\frac{10^{-3}}{10^{-8}} + 1\right)} \approx \sqrt{(2\times 10^{-5})} = 4.47 \times 10^{-3} \text{ M}$$

14. The plot given below shows $p - T$ curves (where p is the pressure and T is the temperature) for two solvents **X** and **Y** and isomolal solutions of NaCl in these solvents. NaCl completely dissociates in both the solvents.



On addition of equal number of moles of a non–volatile solute **S** in equal amount (in kg) of these solvents, the elevation of boiling point of solvent **X** is three times that of solvent **Y**. Solute S is known to undergo dimerization in these solvents. If the degree of dimerization is 0.7 in solvent **Y**, the degree of dimerization in solvent **X** is

Solution

For solvent X, $\Delta T_{bX} = K_{bX}\, m \Rightarrow 2 = 2K_{bX}\, m$ (1)

For solvent Y, $\Delta T_{bY} = K_{bY}\, m \Rightarrow 1 = 2K_{bY}\, m$ (2)

Dividing Eq. (1) by Eq. (2), we get

$$\frac{K_{bX}}{K_{bY}} = 2$$

After adding solute S, molality is the same for both solutions. So, we have

For solvent X, van't Hoff factor $i = 1 - \frac{\alpha}{2}$

$$\Delta T_{bX} = iK_{bX}\, m = \left(1 - \frac{\alpha}{2}\right) K_{bX}\, m \quad (3)$$

For solvent Y, van't Hoff factor $i = 1 - \frac{0.7}{2} = \frac{1.3}{2}$

$$\Delta T_{bY} = iK_{bY}\, m \Rightarrow \left(\frac{1.3}{2}\right) K_{bY}\, m \quad (4)$$

Given that $\Delta T_{bX} = 3\Delta T_{bY}$. Dividing Eq. (3)/(4), we have

$$\frac{\Delta T_{bX}}{\Delta T_{bY}} = \frac{\left(1 - \frac{\alpha}{2}\right) K_{bX}\, m}{\left(\frac{1.3}{2}\right) K_{bY}\, m} \Rightarrow \frac{1}{3} = \frac{2(2-\alpha)}{1.3} \Rightarrow \alpha = 0.05$$

SECTION 3

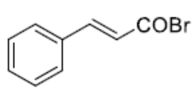
- This section contains **TWO (02)** paragraphs. Based on each paragraph, there are **TWO (02)** questions.
- Each question has **FOUR** options. **ONLY ONE** of these four options corresponds to the correct answer.

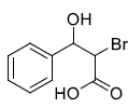
PARAGRAPH "X"

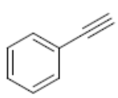
Treatment of benzene with CO/HCl in the presence of anhydrous $AlCl_3$/CuCl followed by reaction with Ac_2O/NaOAc gives compound **X** as the major product. Compound **X** upon reaction with Br_2/Na_2CO_3, followed by heating at 473 **K** with moist KOH furnishes **Y** as the major product. Reaction of **X** with H_2/Pd–C, followed by H_3PO_4 treatment gives **Z** as the major product.

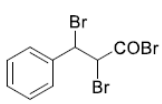
(***There are two questions based on PARAGRAPH "X", the question given below is one of them***)

15. The compound **Y** is

(A) 

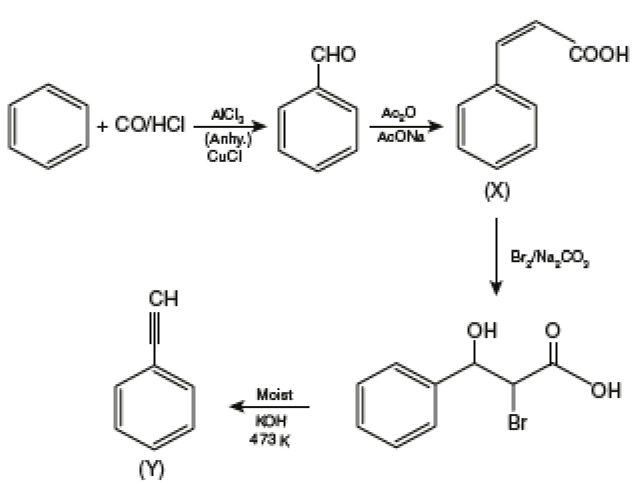
(B) 

(C) 

(D) 

Solution

(C)

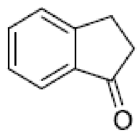


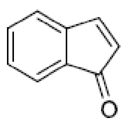
PARAGRAPH "X"

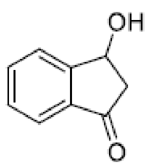
Treatment of benzene with CO/HCl in the presence of anhydrous $AlCl_3$/CuCl followed by reaction with Ac_2O/NaOAc gives compound **X** as the major product. Compound **X** upon reaction with Br_2/Na_2CO_3, followed by heating at 473 **K** with moist KOH furnishes **Y** as the major product. Reaction of **X** with H_2/Pd-C, followed by H_3PO_4 treatment gives **Z** as the major product.

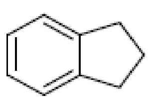
(***There are two questions based on PARAGRAPH "X", the question given below is one of them***)

16. The compound **Z** is

(A) 

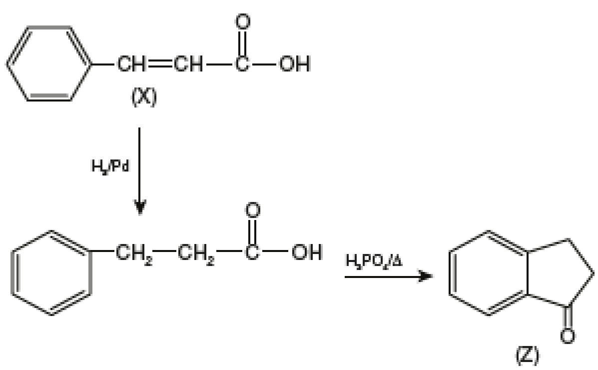
(B) 

(C) 

(D) 

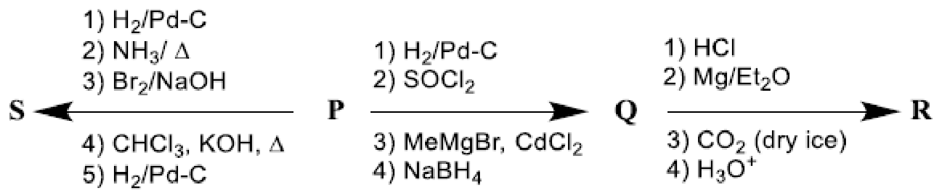
Solution

(C)



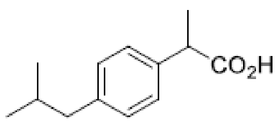
PARAGRAPH "A"

An organic acid **P** ($C_{11}H_{12}O_2$) can easily be oxidized to a dibasic acid which reacts with ethylene glycol to produce a polymer dacron. Upon ozonolysis, **P** gives an aliphatic ketone as one of the products. **P** undergoes the following reaction sequences to furnish **R** *via* **Q**. The compound **P** also undergoes another set of reactions to produce **S**.

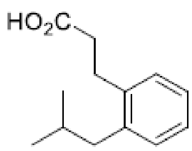


(***There are two questions based on PARAGRAPH "A", the question given below is one of them***)

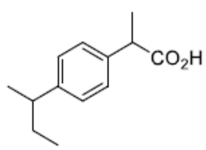
17. The compound **R** is



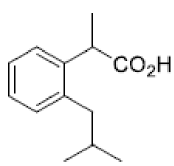
(A)



(B)



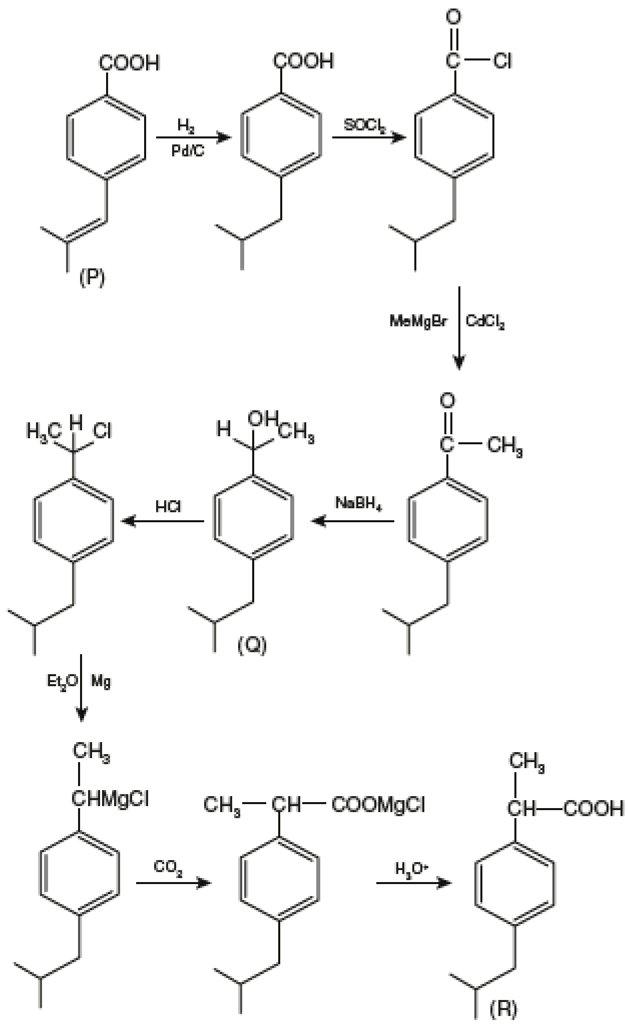
(C)



(D)

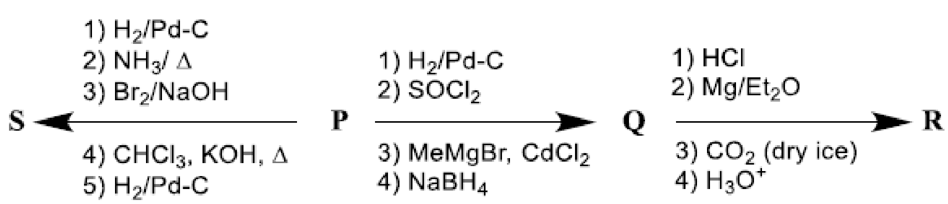
Solution

(A)



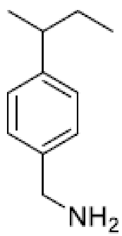
PARAGRAPH "A"

An organic acid **P** ($C_{11}H_{12}O_2$) can easily be oxidized to a dibasic acid which reacts with ethylene glycol to produce a polymer dacron. Upon ozonolysis, **P** gives an aliphatic ketone as one of the products. **P** undergoes the following reaction sequences to furnish **R** *via* **Q**. The compound P also undergoes another set of reactions to produce **S**.

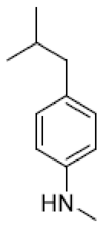


(***There are two questions based on PARAGRAPH "A", the question given below is one of them***)

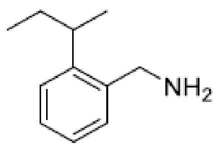
18. The compound **S** is



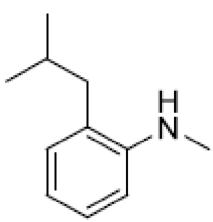
(A)



(B)



(C)



(D)

Solution

(B)