JEE(Advanced) – 2018 TEST PAPER - 1 WITH SOLUTION

(Exam Date: 20-05-2018)

PART-2 : CHEMISTRY

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

Ans. (B,C)

Sol. (A) $NH_4NO_3 \xrightarrow[\text{below } 300°C]{\Delta} N_2O + 2H_2O$

(B) $(NH_4)_2Cr_2O_7 \xrightarrow{\Delta} N_2 + Cr_2O_3 + 4H_2O$

(C) $Ba(N_3)_2 \xrightarrow{\Delta} Ba + 3N_2$

(D) Mg_3N_2 (it does not decompose into N_2)

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

Ans. (B,C)

Sol. (A) $[Fe(CO_5)]$ & $[Ni(CO)_4]$ complexes have 18-electrons in their valence shell.

(B) Carbonyl complexes are predominantly low spin complexes due to strong ligand field.

(C) As electron density increases on metals (with lowering oxidation state on metals), the extent of synergic bonding increases. Hence M–C bond strength increases

(D) While positive charge on metals increases and the extent of synergic bond decreases and hence C–O bond becomes stronger.

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

Ans. (A,B,C)

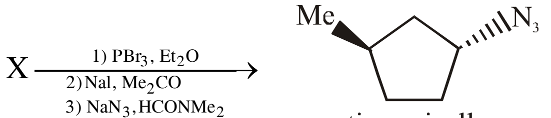
Sol. (A) Bi_2O_5 is metallic oxide but N_2O_5 is non metallic oxide therefore Bi_2O_5 is basic but N_2O_5 is acidic.

(B) In NF_3 , N and F are non metals but BiF_3 , Bi is metal but F is non metal therefore NF_3 is more covalent than BiF_3.

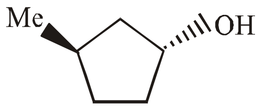
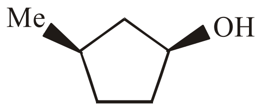
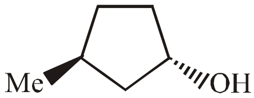
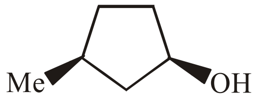
(C) In PH_3 hydrogen bonding is absent but in NH_3 hydrogen bonding is present therefore PH_3 boils at lower temperature than NH_3.

(D) Due to small size in N–N single bond l.p. – l.p. repulsion is more than P–P single bond therefore N–N single bond is weaker than the P–P single bond.

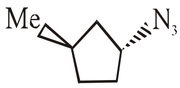
4. In the following reaction sequence, the correct structure(s) of X is (are)

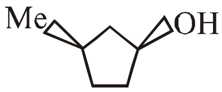


enantiomerically pure

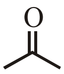
(A)  (B)  (C)  (D) 

Ans. (B)

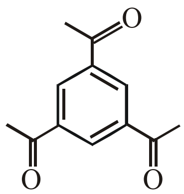
Sol. $X \xrightarrow[\substack{(2)NaI, Me_2C=O \\ (3)NaN_3, HCONMe_2}]{(1)PBr_3 Et_2O}$ 

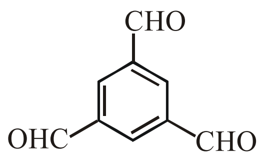
all the three reaction are S_{N^2} so X is 

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

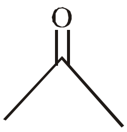
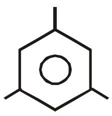
(A)  $\xrightarrow[\Delta]{\text{Conc. } H_2SO_4}$

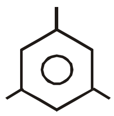
(B) $Me-C\equiv C-H \xrightarrow[873\ K]{\text{heated iron tube}}$

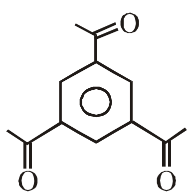
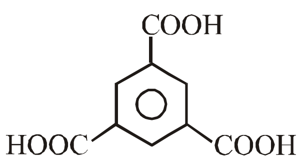
(C)  $\xrightarrow[\text{3) sodalime, } \Delta]{\text{1) } Br_2\text{, NaOH} \quad \text{2) } H_3O^+}$

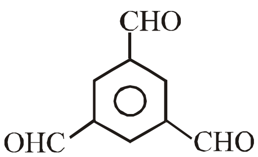
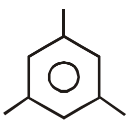
(D)  $\xrightarrow{Zn/Hg,\ HCl}$

Ans. (A,B,D)

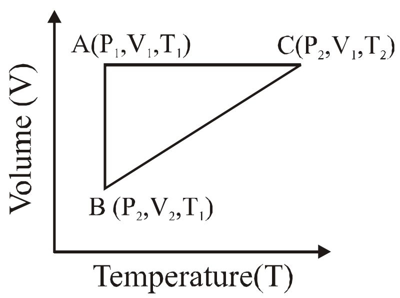
Sol. (A)  $\xrightarrow[\Delta]{ConcH_2SO_4}$ 

(B) $Me-C\equiv C-H \xrightarrow{Fe\Delta}$ 

(C)  $\xrightarrow[(2)H_3O^{\oplus}]{(1)Br_2 NaOH}$  $\xrightarrow[\Delta]{(3)Soda\,lime}$ 

(D)  $\xrightarrow{ZnHg,HCl}$ 

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 $\Delta H_{CA} > \Delta U_{CA}$

Ans. **(B,C)**

Sol. AC $\rightarrow$ Isochoric

AB $\rightarrow$ Isothermal

BC $\rightarrow$ Isobaric

\# $q_{AC} = \Delta U_{BC} = nC_V\ (T_2 - T_1)$

$W_{AB} = nRT_1\ \ln\left(\frac{V_2}{V_1}\right)$ A (wrong)

\# $q_{BC} = \Delta H_{AC} = nC_P\ (T_2 - T_1)$

$W_{BC} = -\ P_2(V_1 - V_2)$ B (correct)

\# $nC_P\ (T_1-T_2) < nC_V(T_1 - T_2)$ C (correct)

$\Delta H_{CA} < \Delta U_{CA}$

\# D (wrong)

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

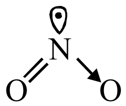
H atom, NO_2 monomer, O_2^- (superoxide), dimeric sulphur in vapour phase,

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

Ans. (1)

Sol.

* H-atom = $\underset{1s^1}{\boxed{1}}$ Paramagnetic

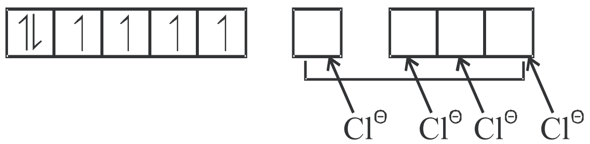
* NO_2 =  odd electron species Paramagnetic

* O_2^- (superoxide) = One unpaired electrons in π^* M.O. Paramagnetic

* S_2 (in vapour phase) = same as O_2, two unpaired e^- s are present in π^* M.O. Paramagnetic

* $Mn_3O_4 = 2\overset{+2}{Mn}O \, . \, \overset{+4}{Mn}O_2$ Paramagnetic

* $(NH_4)_2[FeCl_4]$ = $Fe^{+2} = 3d^6\ 4s^0$

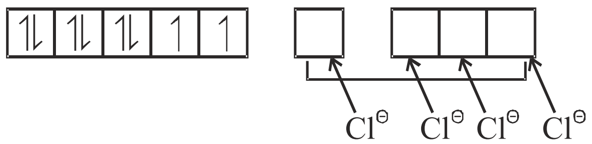


sp^3- hybridisation

Paramagnetic

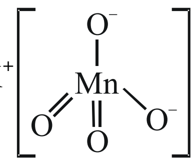
* $(NH_4)_2\ [NiCl_4]$ = $Ni = 3d^8\ 4s^2$

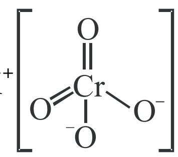
$Ni^{+2} = 3d^8\ 4s^0$



sp^3 - hybridisation

Paramagnetic

* $K_2MnO_4 = 2K^+$ , $Mn^{+6} = [Ar]\ 3d^1$ Paramagnetic

* $K_2CrO_4 = 2K^+$ , $Cr^{+6} = [Ar]\ 3d^0$ Diamagnetic

8. The ammonia prepared by treating ammonium sulphate with calcium hydroxide is completely used by $NiCl_2.6H_2O$ to form a stable coordination compound. Assume that both the reactions are 100% complete. If 1584 g of ammonium sulphate and 952g of $NiCl_2.6H_2O$ 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)

Ans. (2992)

$$\underset{\substack{1584\,g\\=12\text{ mol}}}{(NH_4)_2SO_4} + Ca(OH)_2 \rightarrow \underset{\substack{\text{gypsum }(M=172)\\12\text{ mol}}}{CaSO_4.2H_2O} + \underset{24\,\text{mole}}{2NH_3}$$

$$\underset{952\,g = 4\text{ mol}}{NiCl_2 \cdot 6H_2O} + \underset{24\,\text{mol}}{6NH_3} \rightarrow \underset{\substack{(M=232)\\4\text{ mol}}}{[Ni(NH_3)_6]}Cl_2 + 6H_2O$$

Total mass = 12 × 172 + 4 × 232 = 2992 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____.

Ans. (3)

Sol. $X^{\ominus} \Rightarrow$ O.V.

$M^{+} \Rightarrow$ FCC

	$\mathbf{M^+}$	$\mathbf{X^-}$
(i)	4	1
(ii)	4–3	3+1
(iii)	4 – 3 – 1	3+1
(iv)	1	3

$$Z = \frac{3}{1} = 3$$

10. For the electrochemical cell,

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

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

Ans. (10)

Sol. $Mg(s) + Cu^{2+}(aq) \longrightarrow Mg^{2+}(aq) + Cu(s)$

$E^\circ_{Cell} = 2.70 \qquad E_{Cell} = 2.67 \qquad Mg^{2+} = x\ M$

$\qquad\qquad\qquad\qquad\qquad\qquad Cu^{2+} = 1\ M$

$$E_{Cell} = E^\circ_{Cell} - \frac{RT}{nF}\ln x$$

$$2.67 = 2.70 - \frac{RT}{2F}\ln x$$

$$-0.03 = -\frac{R \times 300}{2F} \times \ln x$$

$$\ln x = \frac{0.03 \times 2}{300} \times \frac{F}{R}$$

$$= \frac{0.03 \times 2 \times 11500}{300 \times 1}$$

$\ln x = 2.30 = \ln(10)$

$x = 10$

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____.

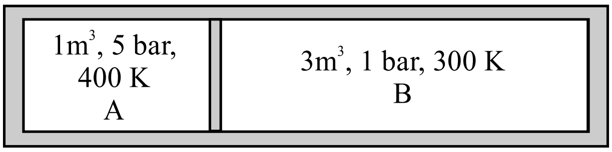


Figure 1

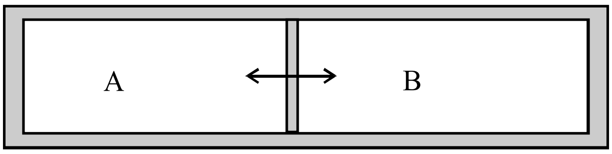


Figure 2

Ans. (2.22)

Sol. $P_1 = 5$ $\quad$ $P_2 = 1$

$v_1 = 1$ $\quad$ $v_2 = 3$

$T_1 = 400$ $\quad$ $T_2 = 300$

$n_1 = \dfrac{5}{400R}$ $\quad$ $n_2 = \dfrac{3}{300R}$

Let volume be (v + x) $\quad$ v = (3–x) $\quad$ 15 – 5x = 4 + 4x

$$\frac{P_A}{T_A} = \frac{P_B}{T_B}$$

$$\Rightarrow \frac{n_{b_1} \times R}{v_{b_1}} = \frac{n_{b_2} \times R}{v_{b_2}}$$

$$\Rightarrow \frac{5}{400(4+x)} = \frac{3}{300R(3-x)}$$

$\Rightarrow$ 5(3 – x) = 4 + 4x

$\Rightarrow$ $x = \dfrac{11}{9}$

$v = 1 + x = 1 + \dfrac{11}{9} = \left(\dfrac{20}{9}\right) = 2.22$

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 vapour pressure 45 Torr. At the same temperature, a new solution of A and B having mole fractions x_A and x_B, respectively, has vapour pressure of 22.5 Torr. The value of x_A/x_B in the new solution is____.

(given that the vapour pressure of pure liquid A is 20 Torr at temperature T)

Ans. (19)

Sol. $45 = P_A^o \times \dfrac{1}{2} + P_B^o \times \dfrac{1}{2}$

$P_A^o + P_B^o = 90$ ....(1)

given $P_A^o = 20$ torr

$P_B^o = 70$ torr

$\Rightarrow$ 22.5 torr = 20 x_A + 70 (1 – x_A)

$\quad$ = 70 – 50 x_A

$x_A = \left(\dfrac{70-22.5}{50}\right) = 0.95$

$x_B = 0.05$

So $\dfrac{x_A}{x_B} = \dfrac{0.95}{0.05} = 19$

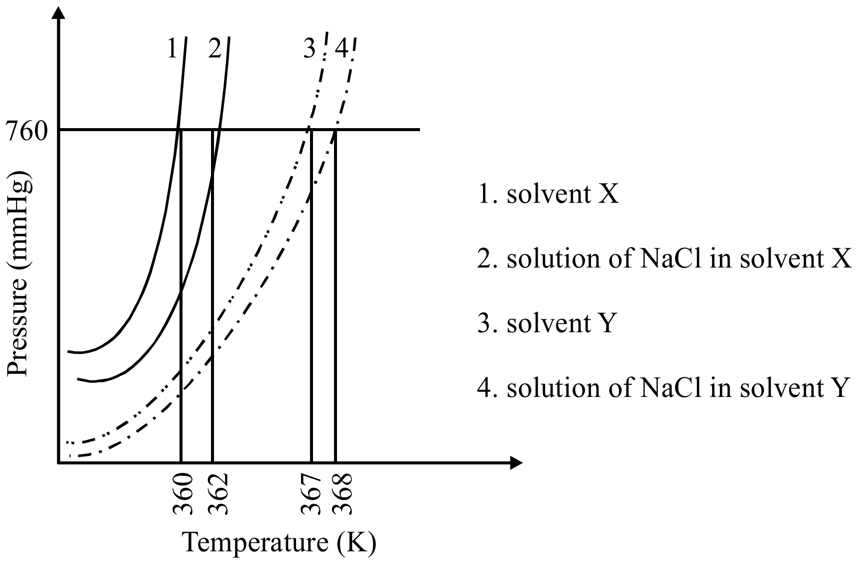
13. The solubility of a salt of weak acid(AB) at pH 3 is $Y \times 10^{-3}$ mol L^{-1}. The value of Y is___.

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

Ans. **(4.47)**

Sol. $S = \sqrt{K_{sp}\left(\frac{[H^+]}{K_a}+1\right)} = \sqrt{2\times10^{-10}\left(\frac{10^{-3}}{10^{-8}}+1\right)} \simeq \sqrt{2\times10^{-5}} = 4.47 \times 10^{-3}$ 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 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 ___.

Ans. **(0.05)**

From graph

For solvent X' $\quad \Delta T_{bx} = 2$

$\Delta T_{bx} = m_{NaCl} \times K_{b(x)}$ ......(1)

For solvent 'Y' $\quad \Delta T_{by} = 1$

$\Delta T_{b(y)} = m_{NaCl} \times K_{b(y)}$ ......(2)

Equation (1)/(2)

$\Rightarrow \frac{K_{b(x)}}{K_{b(y)}} = 2$

For solute S

$$\underset{\substack{1 \\ 1-\alpha}}{2(S)} \rightarrow \underset{\alpha/2}{S_2}$$

$i = (1 - \alpha/2)$

$$\Delta T_{b(x)(s)} = \left(1 - \frac{\alpha_1}{2}\right) K_{b(x)}$$

$$\Delta T_{b(y)(s)} = \left(1 - \frac{\alpha_2}{2}\right) K_{b(y)}$$

Given $\Delta T_{b(x)(s)} = 3\Delta T_{b(y)(s)}$

$$\left(1 - \frac{\alpha_1}{2}\right) K_{b(x)} = 3 \times \left(1 - \frac{\alpha_2}{2}\right) \times k_{b(y)}$$

$$2\left(1 - \frac{\alpha_1}{2}\right) = 3 \left(1 - \frac{\alpha_2}{2}\right)$$

$\alpha_2 = 0.7$

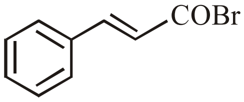
so $\alpha_1 = 0.05$

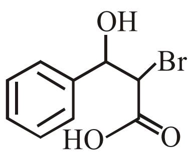
Paragraph "X"

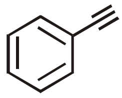
Treatment of benzene with CO/HCl in the presence of anhydrous $AlCl_3$/CuCl followed by reaction with Ac_2O/NaOAc gives compound X as the major product. Compound X upon reaction with Br_2/Na_2CO_3, followed by heating at 473 K with moist KOH furnishes Y as the major product. Reaction of X with H_2/Pd-C,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

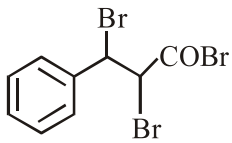
(There are two questions based on PARAGRAPH "X", the question given below is one of them)

15. The compound Y is :-

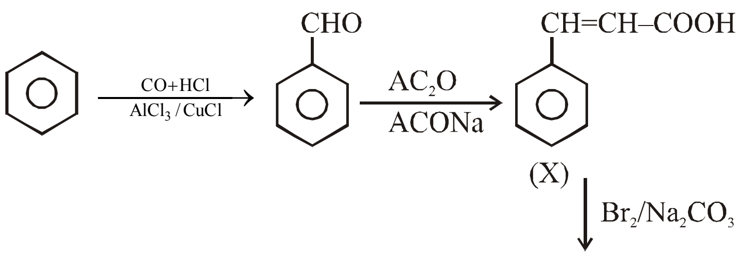
(A) 

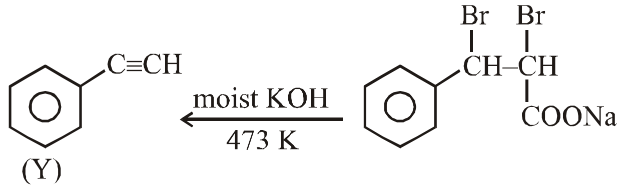
(B) 

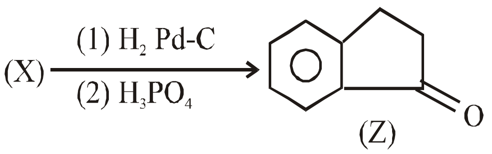
(C) 

(D) 

Ans. **(C)**







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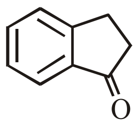
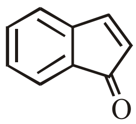
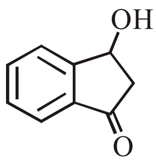
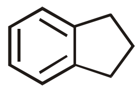
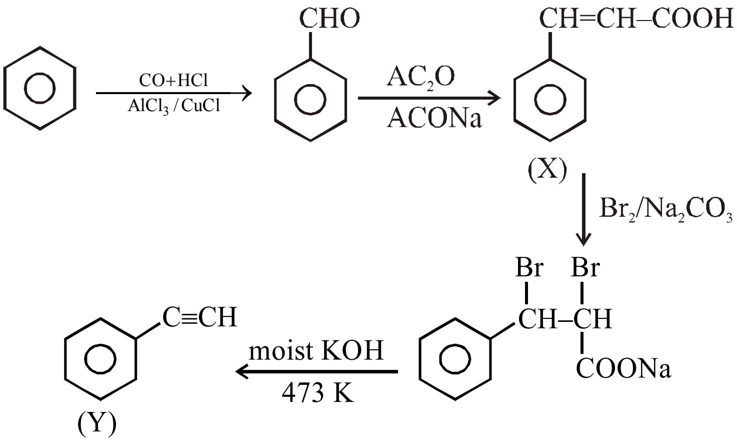
(There are two question based on PARAGARAPH "X", the question given below is one of them)

16. The compound Z is :-

(A)  (B)  (C)  (D) 

Ans. (A)



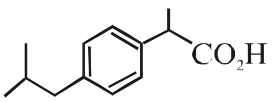
Paragraph "A"

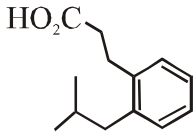
An organic acid P ($C_{11}H_{12}O_2$) can easily be oxidized to a dibasic acid which reacts with ethyleneglycol to produce a polymer dacron. Upon ozonolysis, **P** gives an aliphatic ketone as one of the products. **P** undergoes the following reaction sequences to furnish **R** via **Q.** The compound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

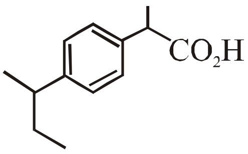
$$S \xleftarrow[\substack{\text{(4) } CHCl_3\text{, KOH, }\Delta \\ \text{(5) } H_2\text{/Pd-C}}]{\substack{\text{(1) } H_2\text{/Pd-C} \\ \text{(2) } NH_3/\Delta \\ \text{(3) } Br_2\text{/NaOH}}} P \xrightarrow[\substack{\text{(3) MeMgBr, } CdCl_2 \\ \text{(4) } NaBH_4}]{\substack{\text{(1) } H_2\text{/Pd-C} \\ \text{(2) } SOCl_2}} Q \xrightarrow[\substack{\text{(3) } CO_2 \text{ (dry ice)} \\ \text{(4) } H_3O^+}]{\substack{\text{(1) HCl} \\ \text{(2) Mg/}Et_2O}} R$$

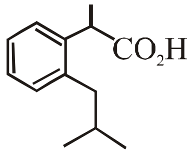
(There are two questions based on PARAGRAPH "A", the question given below is one of them)

17. The compound **R** is

(A) 

(B) 

(C) 

(D) 

Ans. (A)

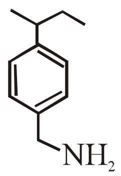
Paragraph "A"

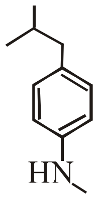
An organic acid P ($C_{11}H_{12}O_2$) can easily be oxidized to a dibasic acid which reacts with ethyleneglycol to produce a polymer dacron. Upon ozonolysis, P gives an aliphatic ketone as one of the products. P undergoes the following reaction sequences to furnish R via Q. The compound P also undergoes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

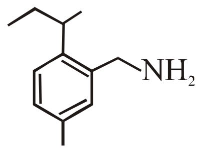
$$S \xleftarrow[\substack{\text{(4) } CHCl_3\text{, KOH, }\Delta \\ \text{(5) } H_2\text{/Pd-C}}]{\substack{\text{(1) } H_2\text{/Pd-C} \\ \text{(2) } NH_3/\Delta \\ \text{(3) } Br_2\text{/NaOH}}} P \xrightarrow[\substack{\text{(3) MeMgBr, } CdCl_2 \\ \text{(4) } NaBH_4}]{\substack{\text{(1) } H_2\text{/Pd-C} \\ \text{(2) } SOCl_2}} Q \xrightarrow[\substack{\text{(3) } CO_2 \text{ (dry ice)} \\ \text{(4) } H_3O^+}]{\substack{\text{(1) HCl} \\ \text{(2) Mg/}Et_2O}} R$$

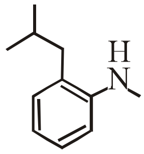
(There are two questions based on PARAGRAPH "A", the question given below is one of them)

18. The compound **S** is

(A) 

(B) 

(C) 

(D) 

Ans. (B)

Solution 17 & 18.