

# CHEMISTRY

## SECTION 1 (Maximum Marks : 21)

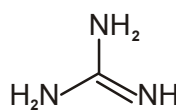
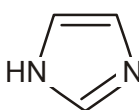
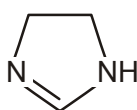
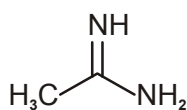
- This section contains **SEVEN** questions
- Each question has **FOUR** options (A), (B), (C) and (D), **ONLY ONE** of these four options is correct
- For each question, darken the bubble corresponding to the correct option in the ORS
- For each question, marks will be awarded in one of the following categories :

Full Marks : +3 If only the bubble corresponding to the correct option is darkened.

Full Marks : 0 If none of the bubbles is darkened.

Negative Marks : -1 In all other cases.

19. The order of basicity among the following compound is :



(A) IV > I > II > III

(B) IV > II > III > I

(C) I > IV > III > II

(D) II > I > IV > III

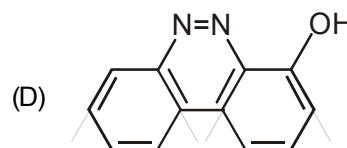
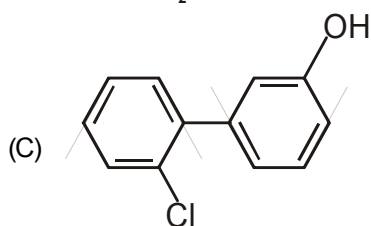
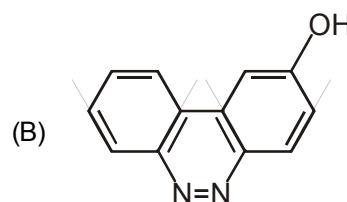
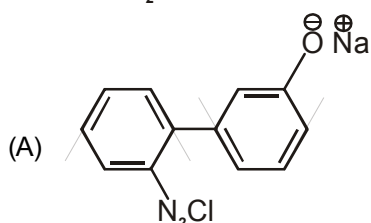
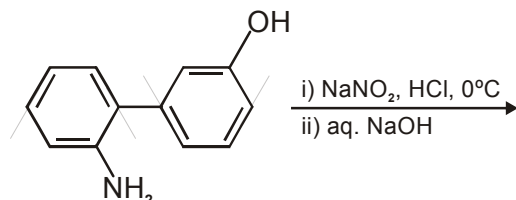
Ans. (A)

Sol. is most basic, because its conjugate acid is having 3 equivalent resonating structures.

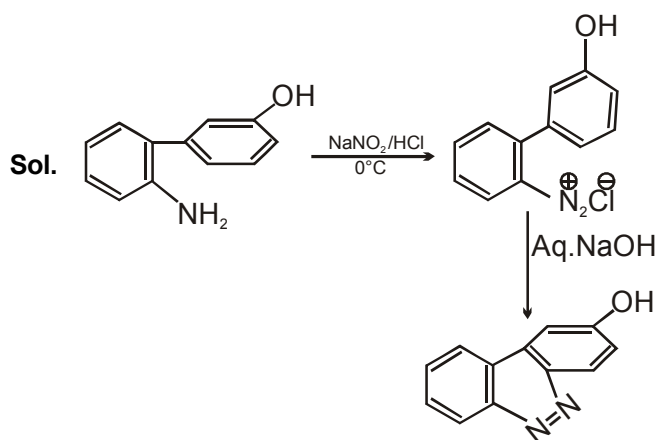
IV

Overall order is  $\leftarrow \begin{matrix} \text{IV} > \text{I} > \text{II} > \text{III} \\ \text{Most basic} \end{matrix}$

20. The major product of the following reaction is :



Ans. (B)

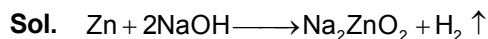


Here 2<sup>nd</sup> step is  $E_{AS}$ , Para position of  $-\text{OH}$  group containing ring is more active for electrophilic substitution.

21. Which of the following combination will produce  $\text{H}_2$  gas ?

- (A) Au metal and  $\text{NaCN}(\text{aq.})$  in the presence of air  
 (B) Zn metal and  $\text{NaOH}(\text{aq.})$   
 (C) Fe metal and conc.  $\text{HNO}_3$   
 (D) Cu metal and conc.  $\text{HNO}_3$

Ans. (B)



22. The standard state Gibbs free energies of formation of C (graphite) and C (diamond) at  $T = 298 \text{ K}$  are :

$$\Delta_f G^\circ[\text{C}(\text{graphite})] = 0 \text{ kJ mol}^{-1}$$

$$\Delta_f G^\circ[\text{C}(\text{diamond})] = 2.9 \text{ kJ mol}^{-1}$$

The standard state means that the pressure should be 1 bar, and substance should be pure at a given temperature. The conversion of graphite [C(graphite)] to diamond [C(diamond)] reduces its volume by  $2 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}$ . If C(graphite) is converted to C(diamond) isothermally at  $T = 298 \text{ K}$ , the pressure at which C(graphite) is in equilibrium with C(diamond), is :

[Useful information :  $1 \text{ J} = 1 \text{ kg m}^2 \text{ s}^{-2}$  ;  $1 \text{ Pa} = 1 \text{ kg m}^{-1} \text{ s}^{-2}$  ;  $1 \text{ bar} = 10^5 \text{ Pa}$ ]

- (A) 14501 bar                      (B) 29001 bar                      (C) 1450 bar                      (D) 58001 bar

Ans. (A)

Sol. At equilibrium  $\Delta G = 0$

$$G_{f(\text{diamond})} = G_{f(\text{graphite})} \quad \dots\dots (i)$$

$$\text{We have } \int_{G^\circ}^G dG = V \int_{P^\circ}^P dP$$

$$G - G^\circ = V(P - P^\circ)$$

$$G = G^\circ + V(P - 1)$$

$$\Delta_f G^\circ = \Delta_f G^\circ_{(\text{diamond})} - \Delta_f G^\circ_{(\text{graphite})} = 2.9 \text{ kJ mol}^{-1}$$

From equation (i)

$$G^\circ_f(\text{diamond}) + V_d(P - 1) = G^\circ_f(\text{graphite}) + V_g(P - 1)$$

$$2.9 \text{ KJ} = (P - 1) (V_g - V_d)$$

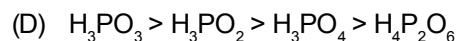
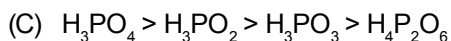
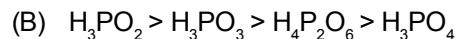
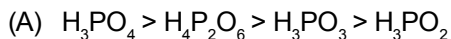
$$2.9 \times 10^3 = (P - 1) \times 2 \times 10^{-6}$$

$$(P - 1) = \frac{2.9 \times 10^3}{2 \times 10^{-6}} = \frac{2.9 \times 10^9}{2} = \frac{29000}{2} \times 10^5 \text{ N/m}^2$$

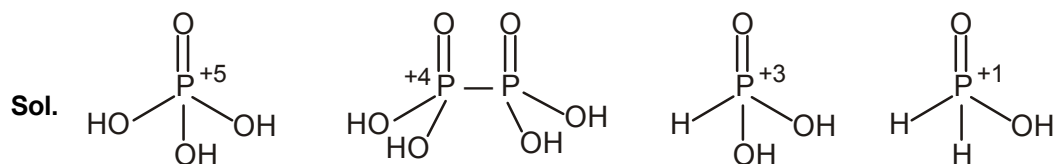
$$(P - 1) = 14500 \text{ bar}$$

$$P = 14501 \text{ bar}$$

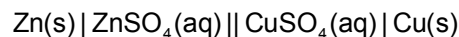
23. The order of the oxidation state of the phosphorus atom in  $\text{H}_3\text{PO}_2$ ,  $\text{H}_3\text{PO}_4$ ,  $\text{H}_3\text{PO}_3$  and  $\text{H}_4\text{P}_2\text{O}_6$  is :



Ans. (A)



24. For the following cell,



when the concentration of  $\text{Zn}^{2+}$  is 10 times the concentration of  $\text{Cu}^{2+}$ , the expression for  $\Delta G$  (in  $\text{J mol}^{-1}$ ) is :

[F is Faraday constant ; R is gas constant ; T is temperature ;  $E^\circ(\text{cell}) = 1.1 \text{ V}$ ]

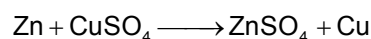
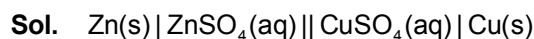
(A)  $2.303 RT - 2.2 F$

(B)  $1.1 F$

(C)  $-2.2 F$

(D)  $2.303 RT + 1.1 F$

Ans. (A)



$$Q = \frac{[\text{ZnSO}_4]}{[\text{CuSO}_4]} = 10$$

$$\Delta G = \Delta G^\circ + 2.303 RT \log Q$$

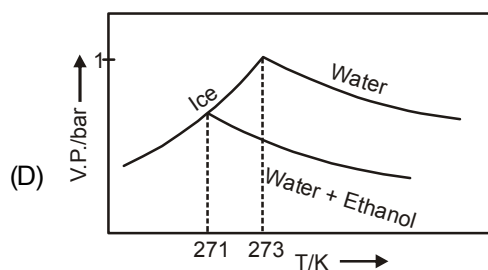
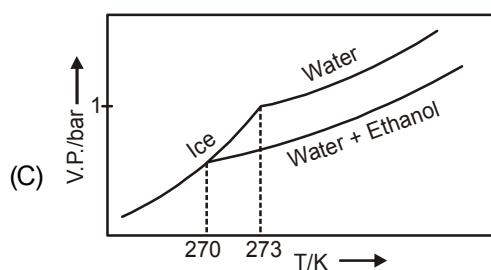
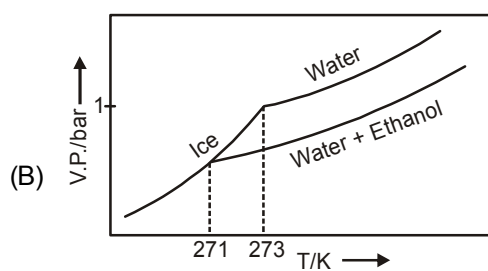
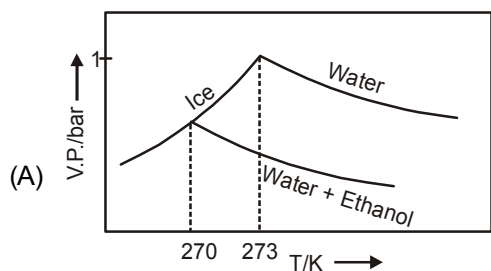
$$= -nFE^\circ + 2.303 RT \log 10$$

$$= -2 \times F \times 1.1 + 2.303 RT$$

$$= 2.303 RT - 2.2 F$$

25. Pure water freezes at 273 K and 1 bar. The addition of 34.5 g of ethanol to 500 g of water changes the freezing point of the solution. Use the freezing point depression constant of water as  $2 \text{ K kg mol}^{-1}$ . The figures shown below represent plots of vapour pressure (V.P.) versus temperature (T). [molecular weight of ethanol is  $46 \text{ g mol}^{-1}$ ]

Among the following, the option representing change in the freezing point is



Ans. (C)

Sol.  $\Delta T_f = K_f \times m$

$$= 2 \times \frac{34.5}{500} \times 1000 = \frac{2 \times 34.5 \times 2}{46} = 3$$

$$T_f(\text{solution}) = 273 - 3 = 270 \text{ K}$$

Also, V.P. increases with increase in temperature.

**SECTION 2 (Maximum Marks : 28)**

- This section contains **SEVEN** questions.
- Each question has **FOUR** options (A), (B), (C) and (D), **ONE OR MORE THAN ONE** of these four options(s) is (are) correct.
- For each question, darken the bubble(s) corresponding to all the correct options(s) in the ORS.
- For each question, marks will be awarded in one of the following categories :  
 Full Marks : +4 If only the bubble(s) corresponding to the correct option(s) is(are) darkened.  
 Partial Marks : +1 For darkening a bubble corresponding to **each correct option**, provided NO incorrect option is darkened.  
 Zero Marks : 0 If none of the bubbles is darkened.  
 Negative Marks : -2 In all other cases.
- For example, if (A), (C) and (D) are all the correct options for a question, darkening all these three will result in +4marks; darkening only (A) and (D) will result in +2 marks; and darkening (A) and (B) will get -2 marks, as a wrong option is also darkened.

- 26.** In a bimolecular reaction, the steric factor P was experimentally determined to be 4.5. The correct option(s) among the following is(are)
- (A) The activation energy of the reaction is unaffected by the value of the steric factor
- (B) Since  $P = 4.5$ , the reaction will not proceed unless an effective catalyst is used
- (C) The value of frequency factor predicted by Arrhenius equation is higher than that determined experimentally
- (D) Experimentally determined value of frequency factor is higher than that predicted by Arrhenius equation.

**Ans. (A,D)**

**Sol.**  $P = \frac{A}{Z}$

When  $P > 1$  experimentally determined value is higher than the predicted value by Arrhenius

$P < 1$ , use of catalyst is required.

$P > 1$ . no need to add catalyst. Activation energy can be experimentally calculated by eliminating steric factor.

- 27.** For a reaction taking place in a container in equilibrium with its surroundings, the effect of temperature on its equilibrium constant K in terms of change in entropy is described by
- (A) With increase in temperature, the value of K for exothermic reaction decreases because favourable change in entropy of the surroundings decreases
- (B) With increase in temperature, the value of K for exothermic reaction decreases because the entropy change of the system is positive
- (C) With increase in temperature, the value of K for endothermic reaction increases because the entropy change of the system is negative
- (D) With increase in temperature, the value of K for endothermic reaction increases because unfavourable change in entropy of the surroundings decreases

**Ans. (A,D)**

**Sol.**  $\Delta S^\circ_{\text{surrounding}} = \frac{-\Delta H^\circ_{\text{system}}}{T}$

$$\Delta G^\circ = (\Delta H^\circ - T\Delta S^\circ) = -RT \ln K \Rightarrow \left( \ln K = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \right)$$

For Exothermic reaction

$$\Delta H^\circ < 0; \Delta S^\circ_{\text{surrounding}} > 0$$

$\Rightarrow$  This reaction is favoured by increase in entropy of surrounding.

$\Rightarrow \uparrow T \Rightarrow (\Delta S^\circ_{\text{surrounding}}) \downarrow \Rightarrow$  (favourable change in entropy of surrounding)  $\downarrow \Rightarrow K \downarrow$

For Endothermic reaction

$$\Delta H^\circ > 0; \Delta S^\circ_{\text{surrounding}} < 0; \Delta S^\circ_{\text{system}} > 0 \text{ for } \Delta G^\circ < 0$$

$\Rightarrow$  This reaction is favoured by increase in entropy of system and not favoured due to decrease in entropy of surrounding.

$\Rightarrow \uparrow T; \Delta S^\circ_{\text{surrounding}} \downarrow \Rightarrow$  (unfavourable change in entropy of the surroundings)  $\downarrow$

$\Rightarrow K \uparrow$

**28.** The correct statement(s) about surface properties is(are)

- (A) Adsorption is accompanied by decrease in enthalpy and decrease in entropy of the system
- (B) Cloud is an emulsion type of colloid in which liquid is dispersed phase and gas is dispersion medium
- (C) The critical temperature of ethane and nitrogen are 563 K and 126 K, respectively. The adsorption of ethane will be more than that of nitrogen on same amount of activated charcoal at a given temperature
- (D) Brownian motion of colloidal particles does not depend on the size of the particles but depends on viscosity of the solution.

**Ans. (A,C)**

**Sol.** (A) In adsorption:  $\Delta H < 0$  (Exothermic)

$$\Delta S < 0$$

(B) Wrong: cloud is not emulsion

(C) correct : high critical temperature means stronger bonding

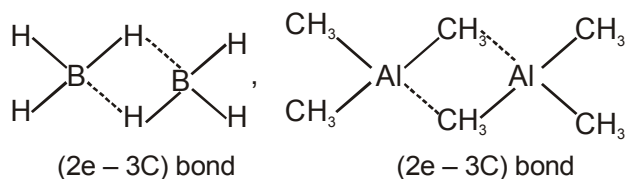
$\Rightarrow$  more adsorption on charcoal

(D) Brownian movement  $\propto \frac{1}{\text{size of dispersed particle}}$

29. Among the following, the correct statement(s) is(are)
- (A)  $\text{AlCl}_3$  has the three-centre two-electron bonds in its dimeric structure
- (B)  $\text{BH}_3$  has the three-centre two-electron bonds in its dimeric structure
- (C)  $\text{Al}(\text{CH}_3)_3$  has the three-centre two-electron bonds in its dimeric structure
- (D) The Lewis acidity of  $\text{BCl}_3$  is greater than that of  $\text{AlCl}_3$

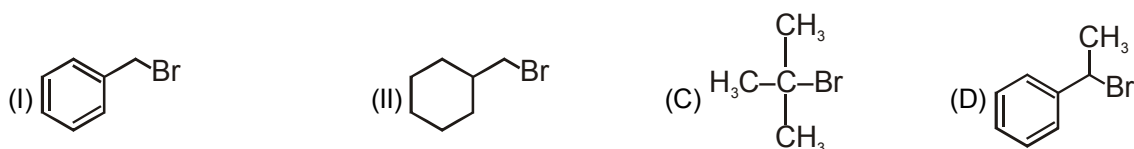
Ans. (B,C,D)

Sol.  $\text{BH}_3$  &  $\text{Al}(\text{CH}_3)_3$  exist in dimeric form due to formation of  $2e-3C$  bond.



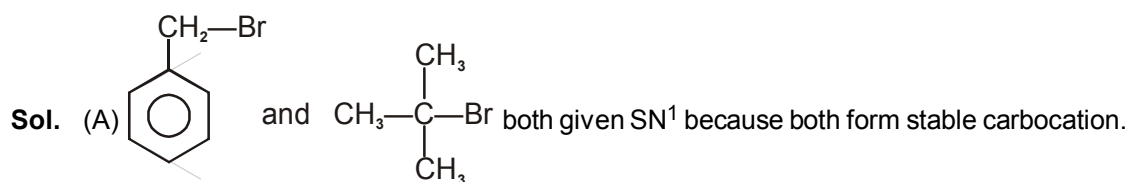
\* Due to smaller size of boron,  $\text{BCl}_3$  is stronger Lewis acid than  $\text{AlCl}_3$ .

30. For the following compounds, the correct statement(s) with respect to nucleophilic substitution reactions is(are)



- (A) (I) and (III) follow  $\text{SN}^1$  mechanism
- (B) Compound (IV) undergoes inversion of configuration
- (C) The order of reactivity for (I), (III) and (IV) is: (IV) > (I) > (III)
- (D) (I) and (II) follow  $\text{SN}^2$  mechanism

Ans. (A, B, D)



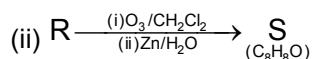
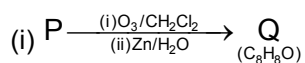
- (B) Being benzylic substrate, a good reactant for  $\text{SN}^2$  hence shows inversion in suitable condition.
- (D) Primary halides and benzylic halides are good substrate for  $\text{SN}^2$ .

31. The option(s) with only amphoteric oxides is(are)
- (A)  $\text{ZnO}$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{PbO}$ ,  $\text{PbO}_2$  (B)  $\text{Cr}_2\text{O}_3$ ,  $\text{CrO}$ ,  $\text{SnO}$ ,  $\text{PbO}$
- (C)  $\text{Cr}_2\text{O}_3$ ,  $\text{BeO}$ ,  $\text{SnO}$ ,  $\text{SnO}_2$  (D)  $\text{NO}$ ,  $\text{B}_2\text{O}_3$ ,  $\text{PbO}$ ,  $\text{SnO}_2$

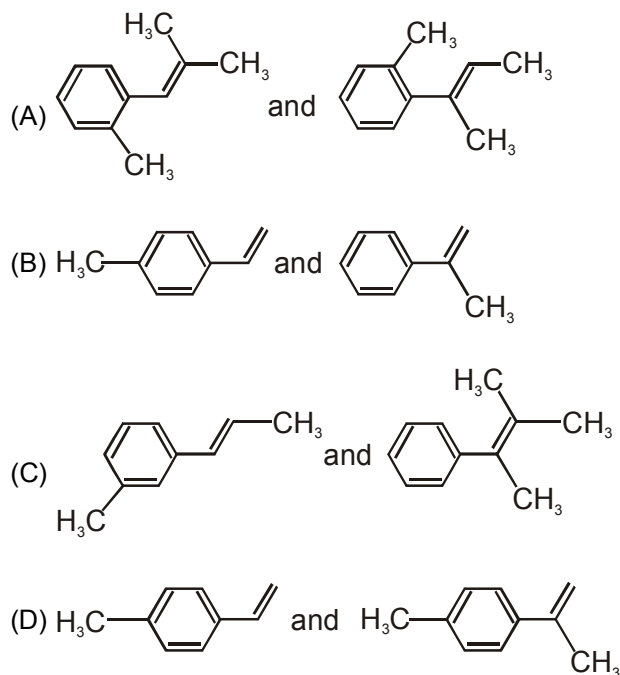
Ans. (A,C)

Sol.  $\text{ZnO}$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{PbO}$ ,  $\text{PbO}_2$ ,  $\text{Cr}_2\text{O}_3$ ,  $\text{BeO}$ ,  $\text{SnO}_2$  and  $\text{SnO}$  are amphoteric oxide.

32. Compounds P and R upon ozonolysis produce Q and S, respectively. The molecular formula of Q and S is  $C_8H_8O$ . Q undergoes Cannizzaro reaction but not haloform reaction, whereas S undergoes haloform reaction but not Cannizzaro reaction.



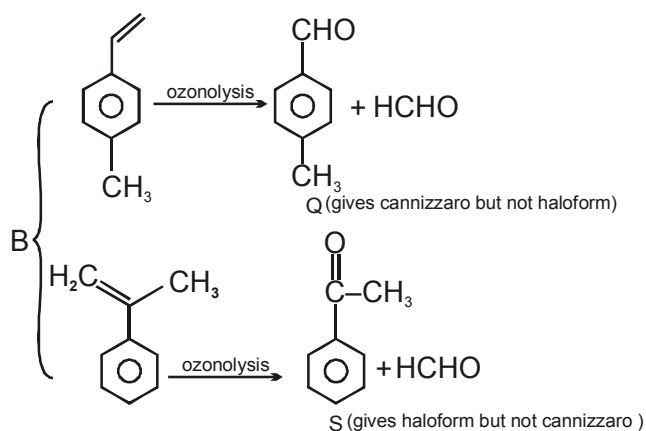
The option(s) with suitable combination of P and R, respectively, is(are)



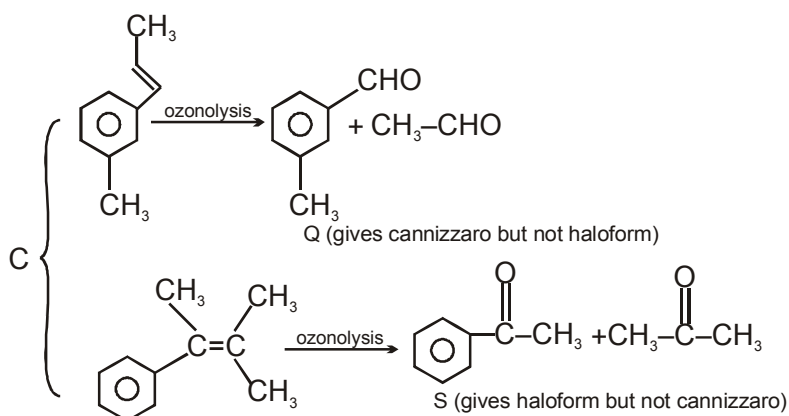
Ans. (B,C)

Sol. P  $\xrightarrow{\text{ozonolysis}}$  Q ( $C_8H_8O$ ) undergo cannizzaro but not haloform.

R  $\xrightarrow{\text{ozonolysis}}$  S ( $C_8H_8O$ ) undergo haloform but not cannizzaro.







### SECTION 3 (Maximum Marks : 12)

- This section contains **TWO** questions
- Based on each paragraph, there are **TWO** questions
- Each question has **FOUR** options (A), (B), (C), and (D). **ONLY ONE** of these four options is correct
- For each question, darken the bubble corresponding to the correct option in the ORS
- For each question, marks will be awarded in one of the following categories:

Full Marks : +3 If only the bubbles corresponding to the correct option is darkened

Zero Marks : 0 In all other cases

#### PARAGRAPH-1

Upon heating  $\text{KClO}_3$  in the presence of catalytic amount of  $\text{MnO}_2$ , a gas W is formed. Excess amount of W reacts with white phosphorus to give X. The reaction of X with pure  $\text{HNO}_3$  gives Y and Z.

33. W and X are, respectively

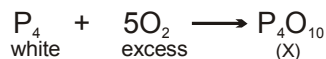
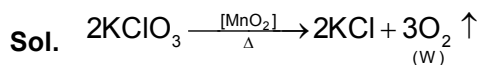
(A)  $\text{O}_3$  and  $\text{P}_4\text{O}_6$

(B)  $\text{O}_2$  and  $\text{P}_4\text{O}_6$

(C)  $\text{O}_2$  and  $\text{P}_4\text{O}_{10}$

(D)  $\text{O}_3$  and  $\text{P}_4\text{O}_{10}$

Ans. (C)



34. Y and Z are, respectively

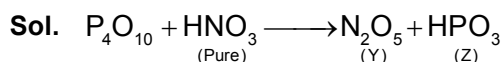
(A)  $\text{N}_2\text{O}_5$  and  $\text{HPO}_3$

(B)  $\text{N}_2\text{O}_3$  and  $\text{H}_3\text{PO}_4$

(C)  $\text{N}_2\text{O}_4$  and  $\text{HPO}_3$

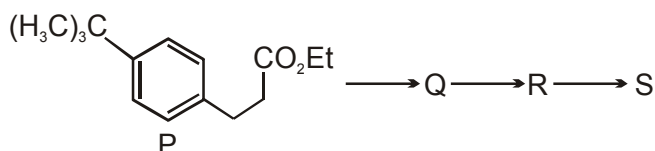
(D)  $\text{N}_2\text{O}_4$  and  $\text{H}_3\text{PO}_3$

Ans. (A)



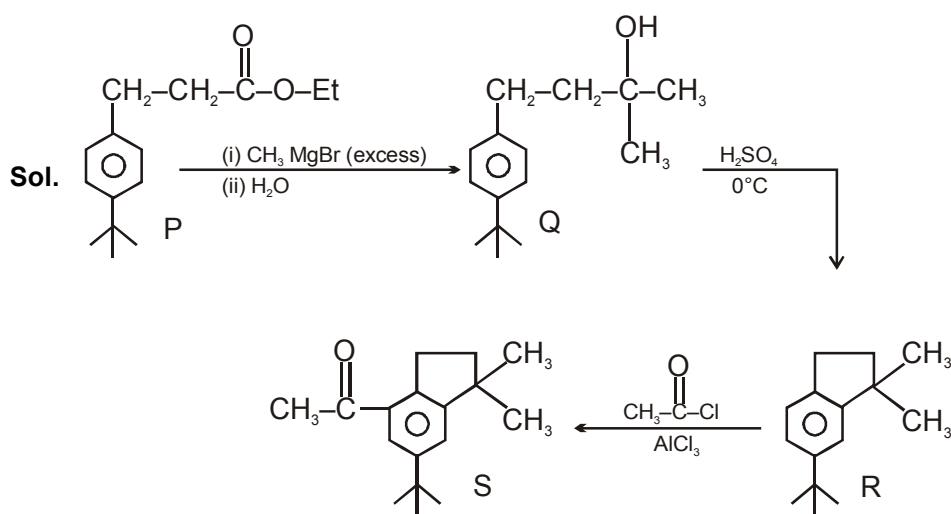
## PARAGRAPH-2

The reaction of compound P with  $\text{CH}_3\text{MgBr}$  (excess) in  $(\text{C}_2\text{H}_5)_2\text{O}$  followed by addition of  $\text{H}_2\text{O}$  gives Q. The compound Q on treatment with  $\text{H}_2\text{SO}_4$  at  $0^\circ\text{C}$  gives R. The reaction of R with  $\text{CH}_3\text{COCl}$  in the presence of anhydrous  $\text{AlCl}_3$  in  $\text{CH}_2\text{Cl}_2$  followed by treatment with  $\text{H}_2\text{O}$  produces compound S. [Et in compound P is ethyl group]

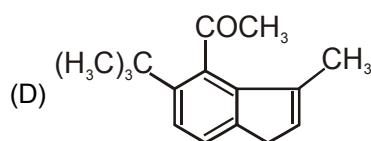
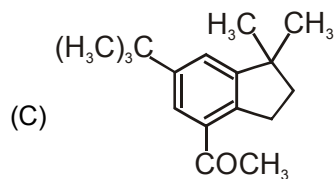
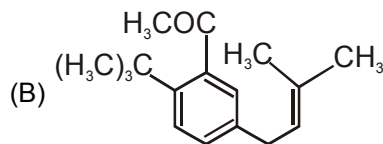
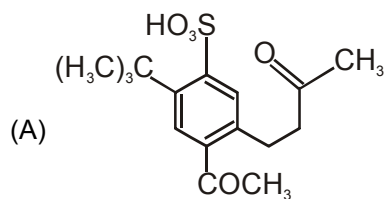


35. The reactions, Q to R and R to S, are
- (A) Dehydration and Friedel-Crafts acylation  
 (B) Friedel-Crafts alkylation, dehydration and Friedel-Crafts acylation  
 (C) Friedel-Crafts alkylation and Friedel-Crafts acylation  
 (D) Aromatic sulfonation and Friedel-Crafts acylation

Ans. (B)



36. The product S is



Ans. (C)