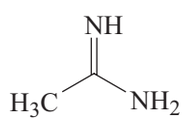
JEE Advanced—2017
Chemistry Paper–II

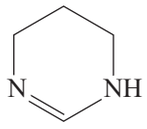
SECTION – I

This section contains **SEVEN** questions. Each question has **FOUR** options (a), (b), (c) and (d). **only ONE** of these **FOUR** options is correct.

1. The order of basicity among the following compounds is



(I)



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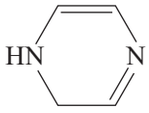
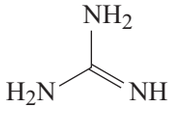


(III)

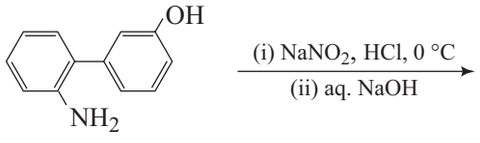


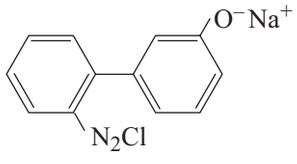
(IV)

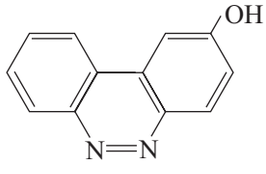
(a) IV > I > II > III (b) IV > II > III > I

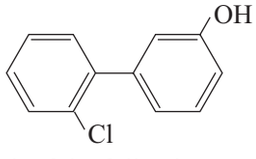
(c) I > IV > III > II (d) II > I > IV > III

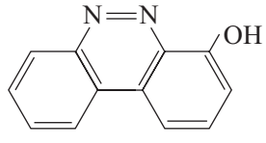
2. The major product of the following reaction is



(a) 

(b) 

(c) 

(d) 

3. Which of the following combination will produce H_2 gas?

(a) Au metal and NaCN(aq) in the presence of air (b) Zn metal and NaOH(aq)

(c) Fe metal and conc. HNO_3 (d) Cu metal and conc. HNO_3

4. The standard state Gibbs free energies of formation of C(graphite) and C(diamond) at $T = 298$ K are $\Delta_f G°$(C, graphite) = 0 kJ mol^{-1} and $\Delta_f G°$(C, diamond) = 2.9 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 C(graphite) to C(diamond) reduces its volume by 2×10^{-6} m^3 mol^{-1}. If C(graphite) is converted to C(diamond) isothermally at $T = 298$ K, the pressure at which C(graphite) is in equilibrium with C(diamond) is (Useful information: 1 J = 1 kg m^2 s^{-1}, 1 Pa = 1 kg m^{-1} s^{-2}, 1 bar = 10^5 Pa.)

(a) 14501 bar (b) 29001 bar (c) 1450 bar (d) 58001 bar

5. The order of the oxidation state of the phosphorus atom in H_3PO_2, H_3PO_4, H_3PO_3 and $H_4P_2O_6$ is

(a) $H_3PO_4 > H_4P_2O_6 > H_3PO_3 > H_3PO_2$ (b) $H_3PO_2 > H_3PO_3 > H_4P_2O_6 > H_3PO_4$

(c) $H_3PO_4 > H_3PO_2 > H_3PO_3 > H_4P_2O_6$ (d) $H_3PO_3 > H_3PO_2 > H_3PO_4 > H_4P_2O_6$

6. For the following cell.

$$Zn\ (s)\ |\ ZnSO_4\ (aq)\ ||\ CuSO_4\ (aq)\ |\ Cu(s)$$

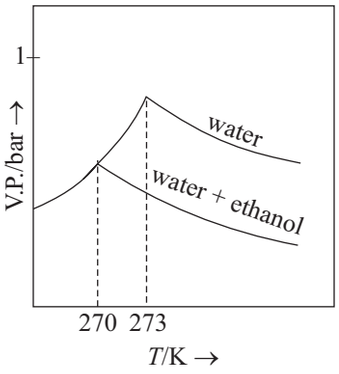
when the concentration of Zn^{2+} ions is 10 times the concentration of Cu^{2+} ions, the expression of ΔG of the cell reaction is

(a) $2.303\ RT - (2.2\ V)\ F$ (b) $(1.1\ V)\ F$ (c) $-(2.2V)\ F$ (d) $2.303\ RT + (1.1\ V)\ F$

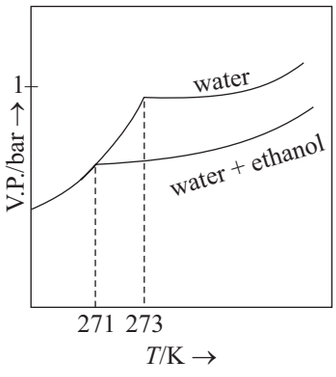
(Where F is Faraday constant, R is gas constant, T is temperature, $E^\circ_{cell} = 1.1$ V.)

7. 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 K kg mol^{-1}. The figures shown below represent plots of vapour pressure (V.P.) versus temperature (T). (Molar mass of ethanol is 46 g mol^{-1}.) Among the following, the option representing changes in the freezing point is

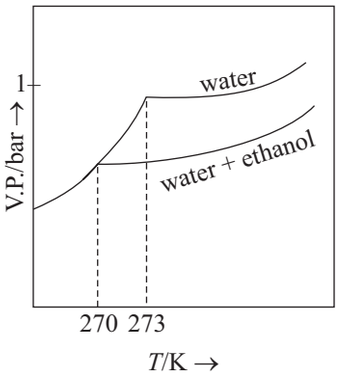
(a)



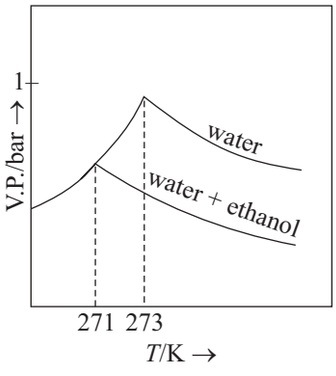
(b)



(c)



(d)



SECTION 2

This section contains **SEVEN** questions. Each question has **FOUR** options (a), (b), (c) and (d). **ONE OR MORE THAN ONE** of these four options is(are) correct.

8. 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 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.

9. 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.

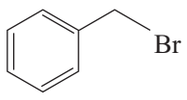
(b) with increases in temperature, the value of K for exothermic reaction decreases because the entropy change of the system is positive.

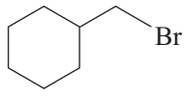
(c) with increase in temperature, the value of K for endothermic reaction increases because the entropy change of the system is negative.
(d) with increase in temperature, the value of K for endothermic reaction increases because unfavourable change in entropy of the surroundings decreases.

10. The correct statement(s) about surface properties is (are):
(a) Adsorption is accompained 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 particle but depends on viscosity of the solution.

11. Among the following the correct statement(s) is (are):
(a) $AlCl_3$ has the three-centre two-electron bonds in its dimeric structure.
(b) BH_3 has the three-centre two-electron bonds in its dimeric structure.
(c) $Al(CH_3)_3$ has the three-centre two-electron bonds in its dimeric structure.
(d) The Lewis acidity of BCl_3 is greater than that of $AlCl_3$.

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


(I)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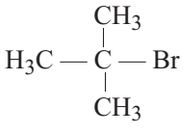
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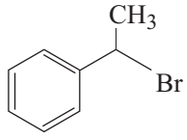

(IV)

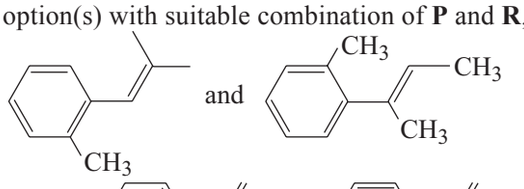
(a) I and III follow S_N1 mechanism
(b) Compound IV undergoes inversion of configuration
(c) The correct order of reactivity for I, III and IV is IV > I > II
(d) I and II follows S_N2 mechanism

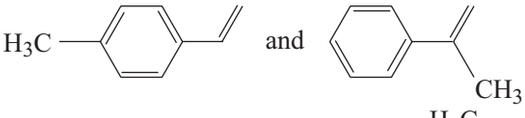
13. The option(s) with only amphoteric oxide is(are):
(a) ZnO, Al_2O_3, PbO, PbO_2
(b) Cr_2O_3, CrO, SnO, PbO
(c) Cr_2O_3, BeO, SnO, SnO_2
(d) NO, B_2O_3, PbO, SnO_2

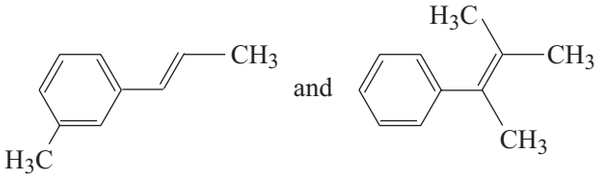
14. Compounds **P** and **R** upon ozonolysis produce **Q** and **S**, respectively. The molecular formula of **Q** and **S** is C_8H_8O. **Q** undergoes Cannizzaro reaction but not haloform reaction, whereas **S** undergoes haloform reaction but not Cannizzaro reaction.

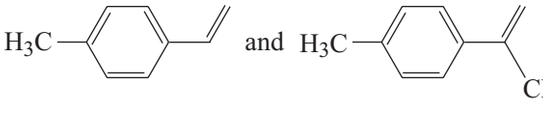
(i) $\mathbf{P} \xrightarrow[\text{(ii) } Zn/H_2O]{\text{(i) } O_3/CH_2Cl_2} \underset{(C_8H_8O)}{\mathbf{Q}}$
(ii) $\mathbf{R} \xrightarrow[\text{(ii) } Zn/H_2O]{\text{(i) } O_3/CH_2Cl_2} \underset{(C_8H_8O)}{\mathbf{S}}$

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

(a) 

(b) 

(c) 

(d) 

SECTION-3

This section contains **TWO** paragraphs. Based on each paragraph, there are **TWO** questions.

Each question has **FOUR** options (a), (b), (c) and (d). **Only ONE** of these options is correct.

Paragraph 1

Upon mixing $KClO_3$ in the presence of catalytic amount of MnO_2, a gas **W** is formed. Excess amount of **W** reacts with phosphorus to give **X**. The reaction of **X** with pure HNO_3 gives **Y** and **Z**.

15. **W** and **X** are, respectively.

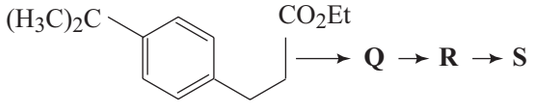
(a) O_3 and P_4O_6 (b) O_2 and P_4O_6 (c) O_2 and P_4O_{10} (d) O_3 and P_4O_{10}

16. **Y** and **Z** are, respectively

(a) N_2O_5 and HPO_3 (b) N_2O_5 and H_3PO_4 (c) N_2O_4 and HPO_3 (d) N_2O_4 and H_3PO_3

Paragraph 2

The reaction of compound **P** with CH_3MgBr (excess) in $(C_2H_5)_2O$ followed by addition of H_2O gives **Q**. The compound **Q** on treatment with H_2SO_4 at 0 °C gives **R**. The reaction of **R** with CH_3COCl in the presence of anhydrous $AlCl_3$ in CH_2Cl_2 followed by treatment with H_2O produces compound **S**. [Et in compound **P** is ethyl group]



(P)

17. The reactions **Q** to **R** and **R** → **S** are

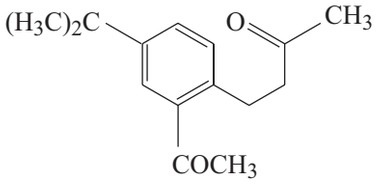
(a) dehydration and Friedel-Crafts acylation

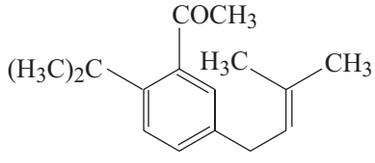
(b) Friedel-Crafts alkylation, dehydration and Friedel-Crafts acylation

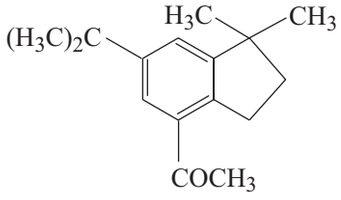
(c) Friedel-Crafts alkylation and Friedel-Crafts acylation

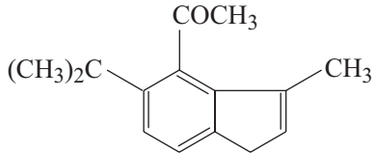
(d) Aromatic sulfonation and Friedel-Crafts acylation

18. The product **S** is

(a) 

(b) 

(c) 

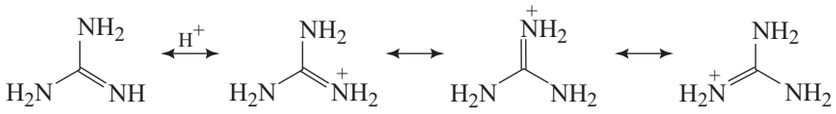
(d) 

ANSWERS

1. (a)	**2.** (b)	**3.** (b)	**4.** (a)	**5.** (a)
6. (a)	**7.** (c)	**8.** (a), (d)	**9.** (a), (d)	**10.** (a), (c)
11. (b), (c), (d)	**12.** (a), (b), (d)	**13.** (a), (c)	**14.** (b), (c)	**15.** (c)
16. (a)	**17.** (c)	**18.** (c)		

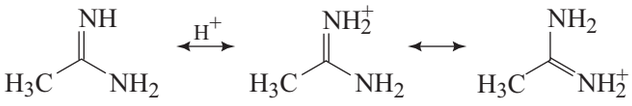
Solutions

1. The molecule IV have maximum basicity. This may be attributed to stability of its conjugate acid due to larger number of resonating structures.



The maximum basicity may also be explained on the basis that the basic site ═NH is attached to two pi-electrons donors which enhances the electron density on the basic site.

The next lesser basic is the molecule I. This involves lesser number of resonating structures in its conjugate acid.

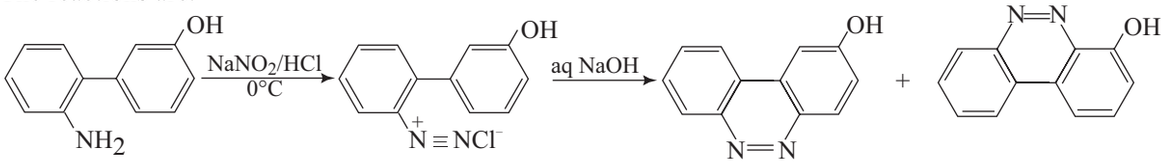


The molecule I has one pi-electrons doner — NH_2 group and one electron-releasing methyl group and thus expected to be lesser basic than molecule IV.

The least basic is the molecule III. The electron pair on nitrogen is delocalised over the whole molecule to make it aromatic. Its lone pair of electrons on nitrogen is not available to make it basic.

Thus, the order of basicity is IV > I > II > III.

2. The reactions are:



(major) (minor)

(more steric hindrance)

3. Zn metal produces H_2 gas with NaOH (aq): $Zn + 2\ NaOH \rightarrow Na_2ZnO_2 + H_2$

The other reactions are:

$$4Au + 8\ NaCN + 2H_2O + O_2 \rightarrow 4Na[Au(CN)_2] + 4\ NaOH$$

$$Fe + 6HNO_3\ (\text{conc.}) \rightarrow Fe(NO_3)_3 + 3NO_2 + 3H_2O$$

$$Cu + 4\ HNO_3\ (\text{conc.}) \rightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O$$

4. $\quad C(\text{graphite}) \longrightarrow C(\text{diamond})$

$\Delta_f G^\circ \quad 0 \qquad\qquad 2.9\ \text{kJ mol}^{-1}$

$$\Delta_r G^\circ = \Delta_f G^\circ(\text{C, diamond}) - \Delta_f G^\circ(\text{C, graphite}) = 2.9\ \text{kJ mol}^{-1} - 0 = 2.9\ \text{kJ mol}^{-1}$$
$$= 2900\ \text{J mol}^{-1}$$

Since $\Delta G = \Delta H - T\Delta S$, we have

$$\Delta G = \Delta(U + pV) - T\Delta S = \Delta U + \Delta(pV) - T\Delta S$$

Since $\Delta U = q + w = q - p\Delta V$ and at constant temperature, $\Delta S = q/T$, we get

$$\Delta G = (q - p\Delta V) + (p\Delta V + V\Delta p) - q = V\Delta p$$

or $$\Delta p = \frac{\Delta G}{V} = \frac{2900\ \text{J mol}^{-1}}{2\times10^{-6}\ \text{m}^3\ \text{mol}^{-1}} = 1450\times10^6\ \text{Pa} = 14500\ \text{bar}$$

i.e. $p_2 = p_1 = 14500$ bar i.e. $p_2 = 14501$ bar ; (since $p_1 = 1$bar)

5. If x is the oxidation state of phosphorus, then we have

$H_3PO_4 \qquad 3\ (+1) + x + 4\ (-2) = 0 \qquad \Rightarrow \qquad x = +5$

$H_4P_2O_6$ $\quad 4(+1) + 2x + 6(-2) = 0 \quad \Rightarrow \quad x = +4$

H_3PO_3 $\quad 3(+1) + x + 3(-2) = 0 \quad \Rightarrow \quad x = +3$

H_3PO_2 $\quad 3(+1) + x + 2(-2) = 0 \quad \Rightarrow \quad x = +1$

Thus, the choice (a) gives the correct order of oxidation state of phosphorus.

6. The cell reaction is $Cu^{2+}(aq) + Zn(s) = Cu(s) + Zn^{2+}(aq)$

The cell potential is

$$E_{cell} = E^\circ_{cell} - \frac{RT}{2F}\ln\left(\frac{[Zn^{2+}]/c^\circ}{[Cu^{2+}]/c^\circ}\right) = 1.1\text{ V} - \frac{2.303RT}{2F}\log\left(\frac{10}{1}\right) = 1.1\text{ V} - \frac{2.303RT}{2F}$$

Since $\Delta G = -nFE_{cell}$, we get

$$-\frac{\Delta G}{2F} = 1.1\text{ V} - \frac{2.303RT}{2F}$$

i.e. $\Delta G = 2.303\ RT - (2.2\text{ V})\ F$

Note: It is desireable to write cell reaction to which ΔG stands for.

7. Vapour pressure of solution increases with increase in temperature. Thus, either choice (b) or choice (c) is correct.

$$\text{Amount of ethanol, } n = \frac{m}{M} = \frac{34.5\text{ g}}{46\text{ g mol}^{-1}} = 0.75\text{ mol}$$

$$\text{Molality of solution, } m = \frac{n}{m_1} = \frac{0.75\text{ mol}}{0.5\text{ kg}} = 1.5\text{ mol kg}^{-1}$$

Depression in freezing point is $-\Delta T_f = K_f m = (2\text{ K kg mol}^{-1})(1.5\text{ mol kg}^{-1}) = 3\text{ K}$

Freezing point of solution, $T_f = T_f^* - \Delta T_f = 273\text{ K} - 3\text{ K} = 270\text{ K}$.

The choice (c) satisfies this requirement.

Note: It is assumed that ethanol is nonvolatile.

8. The activation energy of the reaction is not affected by steric factor (choice a). Since steric factor is more than one, the frequency factor (i.e. frequency of colliding molecules) determined experimentally will be larger that computed from Arrhenius equation.

In fact $Z_{expt} = PZ'$ where Z' is frequency factor computed from Arrhenius equation (choice d).

9. As per Le-Chatelier principle, if the temperature of a reaction at equilibrium is increased, the reaction shifts in a direction so as to decrease the temperature. This decrease in temperature is achieved by releasing less heat in an exothermic reaction and absorbing more heat in an endothermic reaction.

Considering an exothermic reaction

Reactant $\rightleftharpoons$ Product; $\quad \Delta_r H$ = negative

which may be written as

Reactant $\rightleftharpoons$ Product + q

To decrease the value of q, reaction moves towards reactant side causing a decrease in equilibrium constant.

$$K = \frac{[\text{Product}]}{[\text{Reactant}]} = \frac{\text{decrease}}{\text{increase}} = \text{decrease}$$

The heat released in an exothermic reaction causes an increase in entropy of the surroundings. Assuming q does not change significantly, the entropy change ($=q/T$) in the surroundings decreases due to increase in temperature. Since the entropy change is positive, this is referred to as favourable change in entropy and its value decreases with increase in temperature (Choice a).

For an endothermic reaction

Reactant $\rightleftharpoons$ Product; $\quad \Delta_r H$ = positive

which may be written as

Reactant + $q \rightleftharpoons$ Product

With the increase in temperature, absorption of q increases thereby equilibrium is shifted towards product side causing an increase in equilibrium constant

$$K = \frac{[\text{Product}]}{[\text{Reactant}]} = \frac{\text{increase}}{\text{decrease}} = \text{increase}$$

The absorbed heat is supplied by the surroundings, the entropy change of the surroundings will be negative and is referred to as unfavourable change in entorpy. Its value becomes more negative and thus a decrease in entropy of the surroundings will be observed (choice d).

The change in equilibrium constant with change in temperature is independent of the entropy change of the reaction. It depends only on the enthalpy of reaction through the expression

$$\frac{\mathrm{d}\ln K^\circ}{\mathrm{d}T} = \frac{\Delta_r H^\circ}{RT^2}$$

10. Adsorption involves attractions between adsorbent and adsorbate and thus involves a decrease in enthalpy on adsorption. The adsorbate is more ordered after adsorption and is thus accompanied with decrease in entropy.

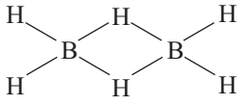
More easily liquefiable gas ethane (which has a higher critical temperature) involves larger intermolecular attractions and thus will exhibit larger adsorption on the same amount of adsorbent.

Cloud belongs to areosol colloid.

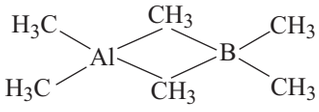
Brownian motion depends on colloidal particle

Thus, the choices (a) and (c) are correct.

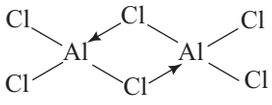
11. The structures of given dimers are:



It has two 3c-2e bonds.



It has two 3c-2e bonds.



No 3c-2e bonds.

BCl_3 is a stronger Lewis acid than $AlCl_3$ due to the presence of more localized p orbital in boron.

12. The main characteristics of S_N1 mechanism are:

(i) Steric hindrance for the incoming nucleophile
(ii) Polar solvent accelerates the substitution
(iii) Chiral starting material ends with the racemization of the products
(iv) Intermediate is carbocation, more stable the carbocation, the faster the S_N1 mechanism

The main characteristics of S_N2 mechanism are

(i) Lesser steric hindrance for the incoming nucleophile
(ii) Aportic solvent accelerates the substitution
(iii) Involves Walden inversion – stereochemistry around carbon atom is inverted

Primary and secondary halides are likely to undergo S_N2 mechanism

Secondary and tertiary halides are likely to undergo S_N1 mechanism

Choice (a) is correct as intermediate cations are stable

Choice (b) is correct as it can follow S_N2 mechanism

Choice (c) is incorrect as compound (III) is expected to have maximum reactivity.

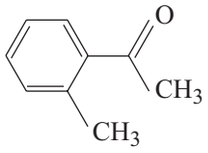
Choice (d) is also correct as the compounds I and II can follow S_N2 mechanism.

13. The amphoteric oxides in the given oxides are: ZnO, Al_2O_3, PbO, PbO_2, Cr_2O_3, BeO, SnO and SnO_2.

Thus, the choices (a) and (c) are correct.

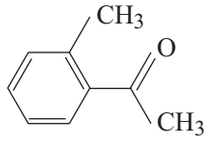
CrO is a basic oxide. NO is a neutral oxide. B_2O_3 is an acidic oxide.

14. The ozonolysis products from **P** and **R** of choice (a) are



(Q)

and

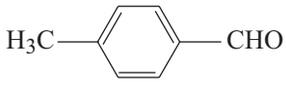


(S)

Gives Cannizzaro reaction due to —CO group with no α-hydrogen.

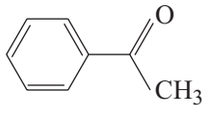
The molecular formula of S is not C_8H_8O.

The ozonolysis products from **P** and **R** of choice (b) are



(Q)

and

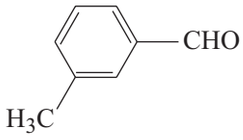


(S)

Gives Cannizzaro reaction due to —CHO group with no α-hydrogen.

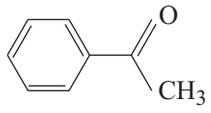
Gives holoform reaction due to $COCH_3$ group.

The ozonolysis products from **P** and **R** of choice (c) are



(Q)

and

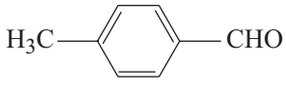


(S)

Gives Cannizzaro reaction due to —CHO group with no α-hydrogen.

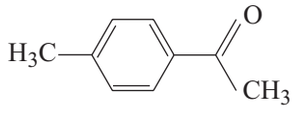
Gives holoform reaction due to —$COCH_3$ Group.

The ozonolysis products from P and R of choice (d) are



(Q)

and



(S)

Gives Cannizzaro reaction due to —CHO group with no α-hydrogen.

The molecular formula of **S** is not C_8H_8O.

Solutions (15 and 16)

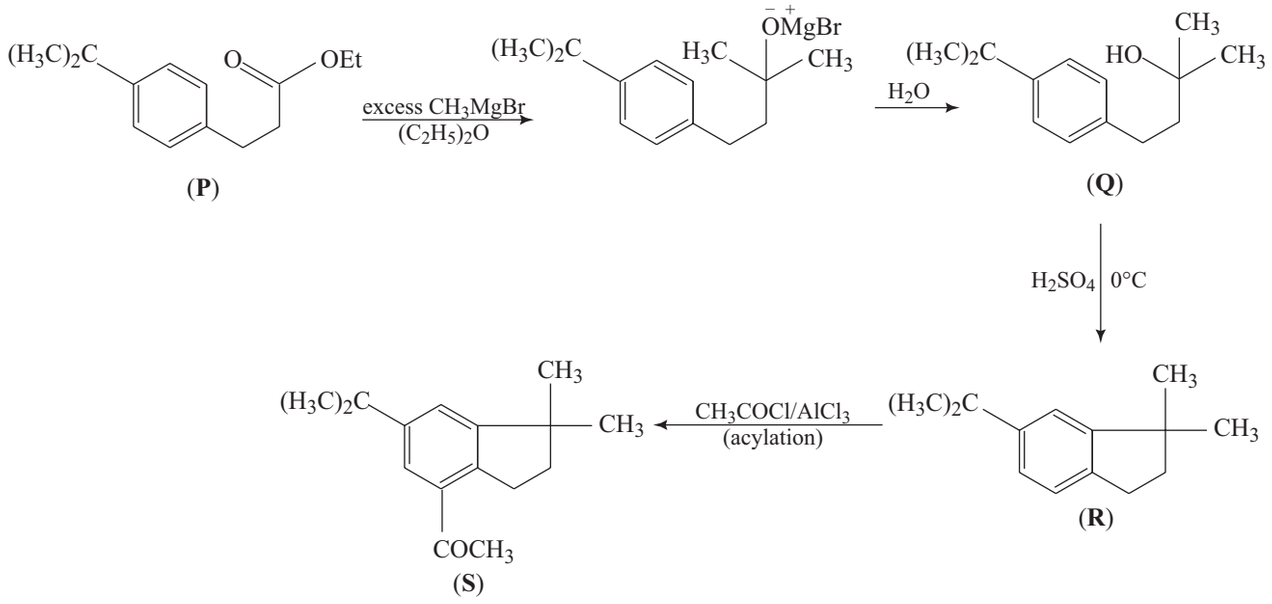
The reactions are:

$$2KClO_3 \xrightarrow{MnO_2} 2KCl + 3O_2$$
(W)

$$P_4 + 5O_2 \rightarrow P_4O_{10}$$
(X)

$$P_4O_{10} + 4\ HNO_3 \rightarrow 2N_2O_5 + 4\ HPO_3$$
(Y) **(Z)**

18. The given reactions are:



17. The conversion of **Q** to **R** involves Friedel-Crafts alkylation and dehydration. The conversion of **R** to **S** involves Friedel-Crafts acylation.

18. The **S** is compound of choice (c).