Examination Papers, 2016

[Foreign Set-I, II, III]

General Instructions: As given in Examination Paper, Delhi 2016.

Set-I (All questions in 3 sets were same)

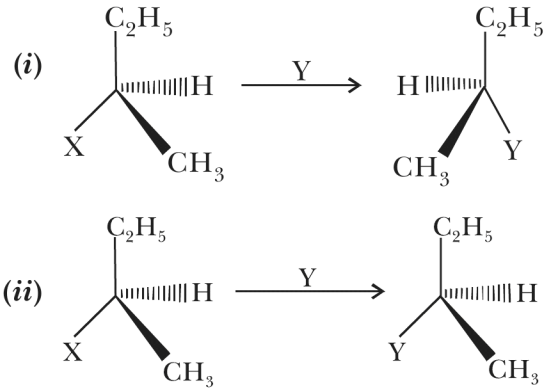
1. Write the main reason for the stability of colloidal sols. [1]

Ans. It is due to the Brownian movement and repulsion between like charged colloidal particles.

2. Glass from ancient monuments appears milky. Why? [1]

Ans. It is due to some crystallization.

3. Which of the following reactions is S_N1 type? [1]



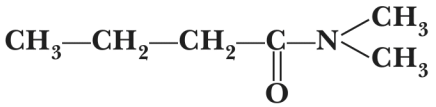
Ans. (*ii*) is S_N1 type.

4. On heating Cu turnings with conc. HNO_3, a brown coloured gas is evolved which on cooling dimerises. Identify the gas. [1]

Ans. Nitrogen dioxide (NO_2).

$$Cu + 4HNO_3(conc.) \longrightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O$$

5. Write the IUPAC name of the given compound. [1]



Ans. N, N-Dimethyl butanamide.

6. When a co-ordination compound $CoCl_3.4NH_3$ is mixed with $AgNO_3$, 1 mole of AgCl is precipitated per mole of the compound. Write

(*i*) Structural formula of the complex

(*ii*) IUPAC name of the complex. **[2]**

Ans. (*i*) $[Co(NH_3)_4Cl_2]Cl$

(*ii*) Tetraamminedichloridocobalt(III)chloride.

7. Show that in a first order reaction, time required for completion of 99.9% is 10 times that of half-life ($t_{½}$) of the reaction. **[2]**

Or

Derive integrated rate equation for rate constant for a first order reaction.

Ans.
$$t_{99.9\%} = \frac{2.303}{k}\log\frac{[R]_0}{\left([R]_0 - \frac{99.9}{100}[R]_0\right)} = \frac{2.303}{k}\log\frac{[R]_0}{0.001[R]_0}$$

$$= \frac{2.303}{k}\log 1000 = \frac{2.303}{k}\times\log 10^3 = \frac{6.909}{k}$$

Also, $$t_{½} = \frac{0.693}{k} \Rightarrow \frac{t_{99.9\%}}{t_{½}} = \frac{6.909}{k}\times\frac{k}{0.693} = 10$$

$\therefore$ $t_{99.9\%} = 10\ t_{1/2}$.

Or

$$R \longrightarrow P$$

$$\text{Rate} = \frac{-d[R]}{dt} \propto [R]'$$

$$\frac{-d[R]}{dt} = k[R]$$

$$\frac{-d[R]}{R} = k\ dt$$

Integrating both sides

$$-\ln[R] = kt + I$$

when $t = 0$, $[R] = [R]_0$ where $[R]_0$ is initial concentration and [R] is final concentration after time '*t*'.

$$-\ln[R]_0 = I$$

$$-\ln[R] = kt - \ln[R]_0$$

$$\ln[R_0] - \ln[R] = kt$$

$$kt = \ln\frac{[R]_0}{[R]}$$

$$k = \frac{2.303}{t}\log\frac{[R]_0}{[R]}$$

8. State Henry's law. Write its one application. What is the effect of temperature on solubility of gases in liquid? [2]

Ans. **Henry's law:** It states that the partial vapour pressure of a gas in vapour phase (p) over the solution is directly proportional to the mole fraction of the gas (x) in the solution.

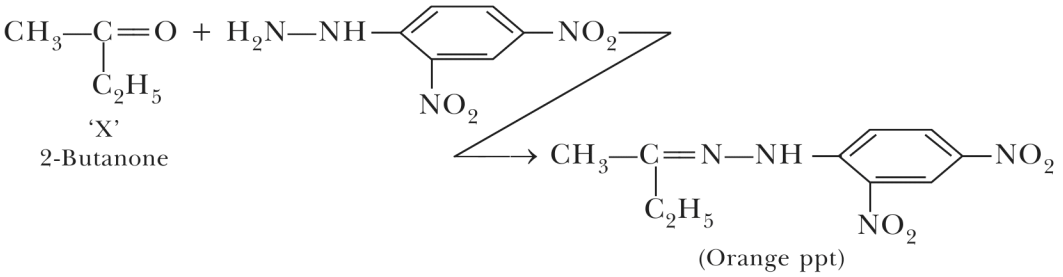
Mathematically, $p = K_H \times x$ where K_H is Henry's law constant, p is partial pressure, 'x' is mole fraction.

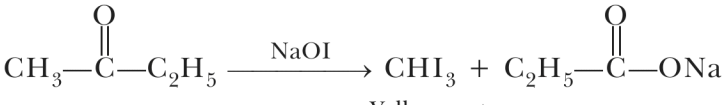
Application: To minimise the painful effects accompanying the decompression of deep sea divers, oxygen diluted with less soluble helium gas is used as breathing gas.

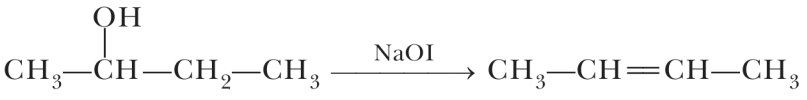
The solubility of gas in liquid decreases with increase in temperature.

9. An organic compound 'X' having molecular formula C_4H_8O gives orange-red ppt. with 2, 4-DNP reagent. It does not reduce Tollens' reagent but gives yellow ppt. of iodoform on heating with NaOI. Compound X on reduction with $LiAlH_4$ gives compound 'Y' which undergoes dehydration reaction on heating with conc. H_2SO_4 to form But-2-ene. Identify the compounds X and Y. [2]

Ans. The compound does not reduce Tollens' reagent, so it is ketone. It gives iodoform test, so it is 2-Butanone. It gives orange red ppt with 2, 4-DNP.







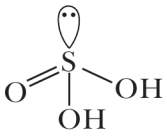
'X' is $CH_3—\overset{\overset{O}{\|}}{C}—C_2H_5$ (Butan-2-one) and 'Y' is $CH_3—\overset{\overset{OH}{|}}{CH}—CH_2—CH_3$ (Butan-2-ol)

10. Write the structures of the following:

(*i*) H_2SO_3

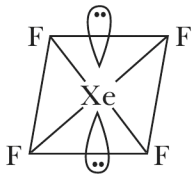
(*ii*) XeF_4 **[2]**

Ans. (*i*)



(H_2SO_3) Trigonal planar

(*ii*)



(XeF_4) Square planar

11. For the first order thermal decomposition reaction, the following data were obtained:

$$C_2H_5Cl(g) \longrightarrow C_2H_4(g) + HCl(g)$$

Time/sec	Total pressure/atm
0	0.30
300	0.50

Calculate the rate constant

(Given: log 2 = 0.301, log 3 = 0.4771, log 4 = 0.6021) **[3]**

Ans. $C_2H_5Cl(g) \longrightarrow C_2H_4(g) + HCl(g)$

p_i 0 0

$p_i - x$ x x

$p_T = p_i - x + x + x$ where p_T is total pressure after time 't', p is initial pressure and '$p_i - x$' is final pressure after time 't'.

$\Rightarrow x = p_T - p_i = 0.50 - 0.30 = 0.20$

$$k = \frac{2.303}{t} \log \frac{p_i}{p_i - x}$$

$$\Rightarrow k = \frac{2.303}{300} \log \frac{0.30}{0.10} \quad [p_i - x = 0.30 - 0.20 = 0.10]$$

$$\Rightarrow k = \frac{2.303}{300} (\log 3)$$

$$\Rightarrow k = \frac{2.303}{300} (0.4771)$$

$$\Rightarrow k = \frac{2.303 \times 0.4771}{300} = \frac{1.0987}{300} = 3.66 \times 10^{-3} \text{ atm}^{-1}$$

12. Give reasons:

(*i*) The α-hydrogen atoms of aldehydes and ketones are acidic in nature.

(*ii*) Propanone is less reactive than ethanal toward addition of HCN.

(*iii*) Benzoic acid does not give Friedel–Crafts reaction. **[3]**

Or

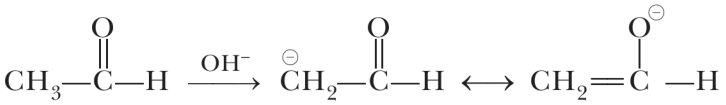
How can you convert?

(*i*) Toluene to Benzaldehyde

(*ii*) Ethanoic acid to 2-chloroethanoic acid

(*iii*) Acetone to Propane

Ans. (*i*) It is because carbanion formed is stabilized by resonance, i.e. stabilization of conjugate base or enolate anion.

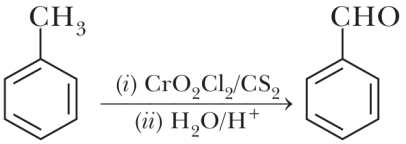


(*ii*) It is due to stearic hindrance and less polarity in propanone than ethanal.

(*iii*) It is because —COOH group is electron withdrawing and deactivating. Also, carboxylic group (Lewis is base due to lone pair on oxygen) gets bonded to catalyst $AlCl_3$ (Lewis acid).

Or

(*i*)



(*ii*) $CH_3COOH \xrightarrow{Cl_2/P_4} \underset{\displaystyle Cl}{\overset{|}{CH_2}}—COOH$

(*iii*) $CH_3—\overset{\displaystyle O}{\overset{\|}{C}}—CH_3 \xrightarrow[\text{conc. HCl}]{Zn(Hg)} \underset{\text{Propane}}{CH_3—CH_2—CH_3}$

(or any other correct method)

13. An element crystallizes in a *fcc* lattice with cell edge of 400 pm. Calculate the density if 200 g of this element contain 2.5×10^{24} atoms. **[3]**

Ans.
$$d = \frac{Z \times M}{a^3 \times N} = \frac{4 \times 200}{(400)^3 \times 10^{-30} \times 2.5 \times 10^{24}} = \frac{4 \times 200}{64 \times 2.5}$$

$$\Rightarrow \quad d = \frac{50}{10} = 5 \text{ g cm}^{-3}$$

14. Define the following terms:

(*i*) Sorption

(*ii*) Zeta potential

(*iii*) Kraft temperature. **[3]**

Ans. (*i*) **Sorption:** It is a process in which adsorption and absorption take place simultaneously, e.g. dying of cotton fibre.

(*ii*) **Zeta potential (Electrokinetic Potential):** The potential difference between the fixed layer and the diffused layer of colloidal solution having opposite charges is called *zeta potential* or *electrokinetic potential*.

(*iii*) **Kraft temperature:** The temperature above which micell formation takes place is called Kraft temperature.

15. Calculate the freezing point of solution when 2 g of Na_2SO_4(M = 142 g mol^{-1}) was dissolved in 50 g of water, assuming Na_2SO_4 undergoes complete ionization. (K_f for water = 1.86 K kg mol^{-1}) **[3]**

Ans. $Na_2SO_4 \longrightarrow 2Na^+ + SO_4^{2-}$

$$i = 3$$

$$\Delta T_f = i\, K_f \times \frac{W_B}{M_B} \times \frac{1000}{W_A}$$

$$= 3 \times 1.86 \times \frac{2}{142} \times \frac{1000}{50}$$

$$= \frac{3 \times 1.86 \times 20}{71} = \frac{111.6}{71} = 1.57\ K$$

Freezing point of solution = Freezing point of solvent – ΔT_f

Freezing point of solution = 273.15 – 1.57 = 271.58 K.

or 0°C – 1.57 = –1.57°C

16. Give reasons:

(*i*) PCl_5 is more covalent than PCl_3.

(*ii*) O—O bond has lower bond dissociation enthalpy than S—S bond.

(*iii*) F_2 is a stronger oxidizing agent than Cl_2. **[3]**

Ans. (*i*) P^{5+} has higher polarising power than P^{3+} ion.

(*ii*) It is due to high inter-electronic repulsion in smaller sized oxygen than sulphur.

(*iii*) It is due to low bond dissociation energy/enthalpy and high hydration enthalpy of F^- ion.

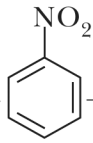
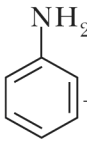
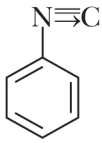
17. Complete the following reactions:

(*i*) $C_6H_5—COO^-NH_4^+ \xrightarrow{\Delta} A \xrightarrow{Br_2/KOH} B \xrightarrow{CH_3COCl/\ pyridine} C$

(*ii*) $C_6H_5N_2^+BF_4^- \xrightarrow[\Delta]{NaNO_2/Cu} A \xrightarrow{Sn/HCl} B \xrightarrow[\Delta]{CHCl_3 + alc.\ KOH} C$ **[3]**

Ans. (*i*) $C_6H_5—COO^-NH_4^+ \xrightarrow{\Delta} \underset{\text{'A'}}{C_6H_5CONH_2} \xrightarrow{Br_2/KOH} \underset{\text{'B'}}{C_6H_5NH_2}$

$\xrightarrow{CH_3COCl/pyridine}$ $C_6H_5NHCOCH_3$ 'C'

(*ii*) $C_6H_5N_2^+BF_4^- \xrightarrow[\Delta]{NaNO_2/Cu}$  'A' $\xrightarrow{Sn/HCl}$  'B' $\xrightarrow[\Delta]{CHCl_3 + alc.\ KOH}$  'C'

18. Write the name of monomers and their structures in the following:

(*i*) Buna–N

(*ii*) PVC

(*iii*) Neoprene **[3]**

Ans. (*i*) **Buna-N:** Buta-1,3-diene and vinyl cyanide.

$CH_2=CH—CH=CH_2$ and $CH_2=CH—CN$

(*ii*) Vinyl chloride, $CH_2=CHCl$

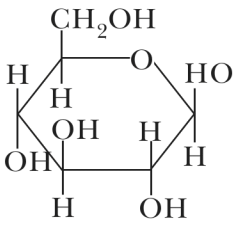
(*iii*) $CH_2=\underset{\displaystyle Cl}{\underset{|}{C}}—CH=CH_2$

Chloroprene (2-chloro buta 1, 3-diene)

19. (*i*) Draw the pyranose structure of glucose.

(*ii*) What type of linkage is present in proteins?

(*iii*) Give one example each for water-soluble vitamins and fat-soluble vitamins. **[3]**

Ans. (*i*) 

(*ii*) Peptide bond/—$\overset{\overset{O}{\|}}{C}$—NH bond.

(*iii*) Vitamins B and C are water soluble.

Vitamins 'A', D, E, K are fat soluble.

20. (*a*) For the complex $[Fe(CO)_5]$, write the hybridization, magnetic character and spin of the complex. (At. number: Fe = 26)

(*b*) Define crystal field splitting energy. [3]

Ans. (*a*) It has dsp^3 hybridization and diamagnetic. It is low spin complex.

(*b*) The energy used to split degenerate *d*-orbital due to the presence of ligands in a definite geometry is called crystal field splitting energy.

21. Write the role of

(*i*) I_2 in the van Arkel method of refining.

(*ii*) Cryolite in the extraction of aluminium.

(*iii*) Dilute NaCN in the extraction of silver. [3]

Ans. (*i*) Iodine is heated with Zr or Ti to form a volatile compound which on further heating decompose to give pure Zr or Ti.

OR

$$\underset{\text{Impure}}{Zr} + 2I_2 \longrightarrow \underset{\text{Volatile}}{ZrI_4}$$

$$ZrI_4 \xrightarrow{1800\ K} \underset{\text{Pure}}{Zr} + 2I_2$$

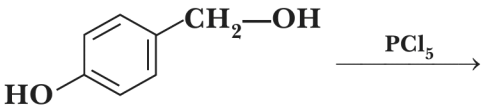
(*ii*) Cryolite lowers the melting point of alumina mixture. It acts as a solvent. It increases electrical conductivity.

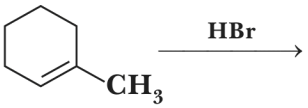
(*iii*) NaCN is used in the formation of complex in pressure of O_2 for leaching of crude Ag

OR

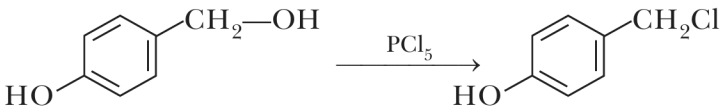
$$4Ag\ (s) + 8CN^- + 2H_2O + O_2\ (g) \longrightarrow 4[Ag(CN)_2]^- + 4OH^-$$

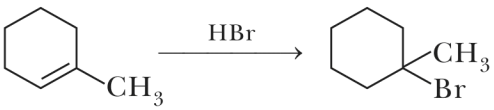
22. **Write the major products(s) in the following reactions:** [3]

(*i*) 

(*ii*) 

(*iii*) $CH_3CH_2Cl \xrightarrow{KNO_2} ?$

Ans. (*i*) 

(*ii*) 

(*iii*) $CH_3CH_2Cl \xrightarrow{KNO_2} CH_3CH_2—O—N=O$

23. **Due to hectic and busy schedule, Mr. Awasthi made his life full of tensions and anxiety. He started taking sleeping pills to overcome the depression without consulting the doctor. Mr. Roy, a close friend of Mr. Awasthi, advised him to stop taking sleeping pills and suggested to change his lifestyle by doing Yoga, meditation and some physical exercise. Mr. Awasthi followed his friend's advice and after few days he started feeling better.**

After reading the above passage, answer the following:

(*i*) What are the values (at least two) displayed by Mr. Roy?

(*ii*) Why it is not advisable to take sleeping pills without consulting doctor?

(*iii*) What are tranquilizers? Give two examples. [4]

Ans. (*i*) Caring, responsible, concerned, compassionate, kind. (*Any two*)

(*ii*) It is because higher doses may be harmful and even fatal.

(*iii*) Tranquilizers are a class of chemical compounds used for the treatment of stress or even metal diseases, e.g. chlordiazepoxide, equanil, valium.

24. **(*a*) Calculate ΔG° and log K_c for the following reaction at 298 K:**

$2Cr(s) + 3Fe^{2+}(aq) \longrightarrow 2Cr^{3+}(aq) + 3Fe(s)$

Given : $E^\circ_{cell} = 0.30$ V

(*b*) Using the E° values of A and B, predict which is better for coating the surface of iron [$E°(Fe^{2+}|Fe) = -0.44$ V] to prevent corrosion and why?

Given: $E°(A^{2+}|A) = -2.37$ V : $E°(B^{2+}|B) = -0.14$ V **[5]**

Or

(*a*) The conductivity of 0.001 mol L^{-1} solution of CH_3COOH is 3.905×10^{-5} S cm^{-1}. Calculate its molar conductivity and degree of dissociation (α).

Given: $\lambda°(H^+) = 349.6$ S cm^2 mol^{-1} and $\lambda°(CH_3COO^-) = 40.9$ S cm^2 mol^{-1}.

(*b*) What type of battery is lead storage battery? Write the overall reaction occurring in lead storage battery.

Ans. (*a*) $E°_{cell} = 0.30$ V, F = 96500 C mol^{-1}

$$2Cr\,(s) \longrightarrow 2Cr^{3+}\,(aq) + 6e^-$$
$$6e^- + 3Fe^{2+} \longrightarrow 3Fe\,(s)$$
$$2Cr\,(s) + 3Fe^{2+} \longrightarrow 2Cr^{3+} + 3Fe$$

$n = 6$

$\Delta_r G° = -nE°_{cell}\,F = -6 \times 0.30\text{ V} \times 96500\text{ C mol}^{-1}$

$= -173{,}700$ J/mol $= -173.7$ kJ/mol

$$\log K_C = \frac{nE°_{cell}}{0.0591}$$

$$\log K_C = \frac{6 \times 0.30}{0.0591}$$

$\log K_C = 30.5 \Rightarrow K_C = \text{Anitlog } 30.5$

$\Rightarrow K_C = 3.162 \times 10^{30}$

(*b*) 'A' is better for coating the surface of iron because it has lower value of reduction potential, acts as anode and Fe acts as cathode. 'A' oxidises in preference to Fe to prevent corrosion.

$E°_{cell}$ is positive and 'A' oxidises itself to prevent corrosion of Fe.

Or

(*a*)
$$\Lambda_m = \frac{1000\,\kappa}{C} = \frac{1000 \times 3.905 \times 10^{-5}}{0.001} = 39.05\text{ S cm}^2\text{ mol}^{-1}$$

$$\Lambda° = \lambda°_{H^+} + \lambda°_{CH_3COO^-} = (349.6 + 40.9)\text{ cm}^2\text{ mol}^{-1}$$

$\Lambda° = 390.5$ S cm^2 mol^{-1}

$$\alpha = \frac{\Lambda_m}{\Lambda°} = \frac{39.05}{390.5} = 0.1$$

$\alpha = 0.1$ or $0.1 \times 100 = 10\%$

(*b*) Secondary cell or rechargeable battery

$Pb\ (s) + PbO_2\ (s) + 2SO_4^{2-} + 4H^+\ (aq) \longrightarrow 2PbSO_4\ (s) + 2H_2O\ (l)$

25. (*a*) Account for the following:

(*i*) Mn_2O_7 is acidic whereas MnO is basic.

(*ii*) Though copper has completely filled *d*-orbital (d^{10}) yet it is considered as a transition metal.

(*iii*) Actinoids show wide range of oxidation states.

(*b*) Write the preparation of potassium permanganate from pyrolusite ore (MnO_2). **[5]**

Or

(*a*) The elements of 3*d* transition series are given as:

Sc Ti V Cr Mn Fe Co Ni Cu Zn

Answer the following:

(*i*) Which element has the highest m.p. and why?

(*ii*) Which element is a strong oxidizing agent in +3 oxidation state and why?

(*iii*) Which element is soft and why?

(*b*) Write the equation involved in the preparation of Potassium dichromate from Sodium chromate (Na_2CrO_4).

Ans. (*a*) (*i*) It is because of higher oxidation +7 in Mn_2O_7 than +2 in MnO.

(*ii*) It is due to presence of unpaired electron in 3*d* orbital in its +2 oxidation state.

(*iii*) It is because 5*f*, 6*d* and 7*s* orbitals.

(*b*) $2MnO_2 + 4KOH + O_2 \longrightarrow 2K_2MnO_4 + 2H_2O$

$3MnO_4^{2-} + 4H^+ \longrightarrow 2MnO_4^- + MnO_2 + 2H_2O$

or $MnO_4^{2-} \xrightarrow{\text{electrolysis}} MnO_4^- + e^-$

Or

(*a*) (*i*) Cr. It is due to presence of maximum number of electrons forming strong metallic bonds.

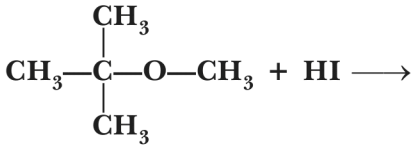
(*ii*) Mn^{3+} is a strong oxidising agent because it can gain one electron to form Mn^{2+} which is more stable due to half-field *d*-orbital.

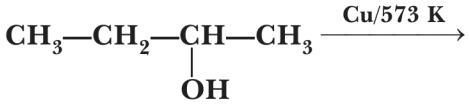
(*iii*) Zn, because it does not have unpaired electron and has weak metallic bonds.

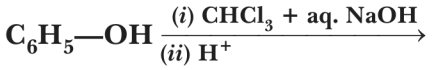
(*b*) $2Na_2CrO_4 + H_2SO_4 \longrightarrow Na_2Cr_2O_7 + Na_2SO_4 + H_2O$

$Na_2Cr_2O_7 + 2KCl \longrightarrow K_2Cr_2O_7 + 2NaCl$

26. (*a*) Write the major product(s) in each of the following reactions:

(*i*) 

(*ii*) 

(*iii*) 

(*b*) Write the chemical reaction involved in the following reactions:

(*i*) Kolbe's reaction

(*ii*) Friedel–Crafts acetylation of anisole **[5]**

Or

(*a*) What happens when

(*i*) phenol reacts with Bromine water?

(*ii*) ethanol reacts with CH_3COCl/pyridine?

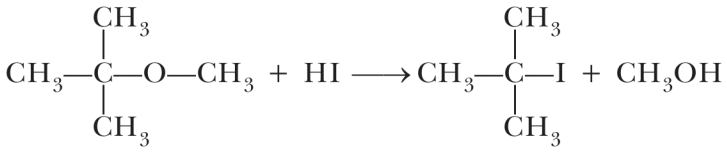
(*iii*) anisole reacts with HI?

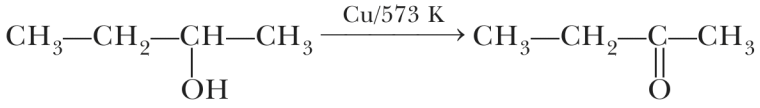
Write the chemical equations involved in the above reactions.

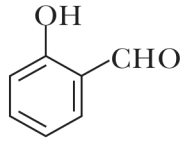
(*b*) Distinguish between:

(*i*) Ethanol and phenol

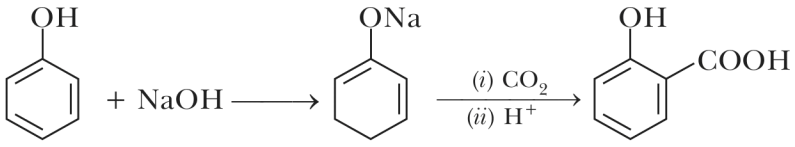
(*ii*) Propan-2-ol and 2-methylpropan-2-ol

Ans. (*a*) (*i*) 

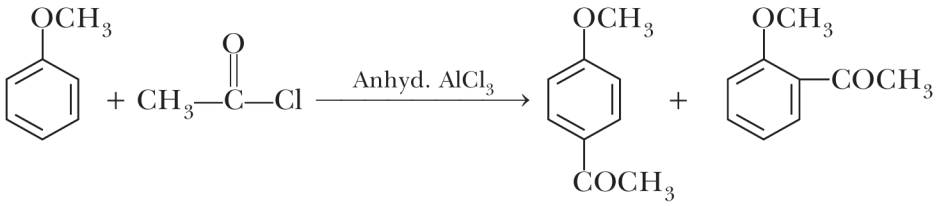
(*ii*) 

(*iii*) $C_6H_5—OH \xrightarrow[(ii)\ H^+]{(i)\ CHCl_3 + \text{aq. NaOH}}$ 

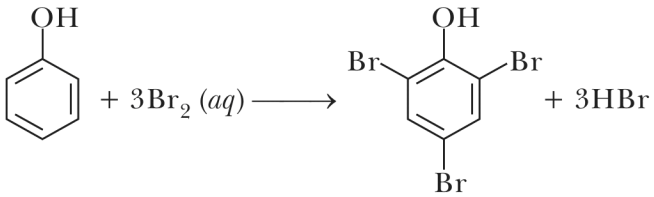
(*b*) (*i*) **Kolbe's reaction:**



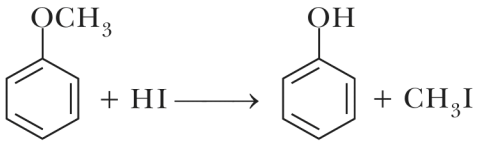
(*ii*) **Friedel–Crafts acetylation of anisole:**



Or

(*a*) (*i*) 

(*ii*) $C_2H_5OH + CH_3—\overset{\overset{O}{\|}}{C}—Cl \xrightarrow{\text{Pyridine}} CH_3—CH_2—O—\overset{\overset{O}{\|}}{C}—CH_3$

(*iii*) 

(*b*) (*i*) Warm each compound with iodine and sodium hydroxide. Phenol will not give yellow ppt., whereas ethanol gives yellow precipitate of iodoform.

(*ii*) Add Lucas reagent (Conc. HCl + $ZnCl_2$). Propan-2-ol will give turbidity after 5 minutes, whereas 2-methyl-propan-2ol will give turbidity immediately.