

CBSE Class 12 Chemistry Question Paper 2022 with Solution PDF-Set 56-2-2

Question Paper with Solutions

Conducted by the Central Board of Secondary Education (CBSE)



Time Allowed: 2 hours

Maximum Marks: 35

General Instructions

- (i) This question paper contains **12** questions. **All** questions are compulsory.
- (ii) This question paper is divided into **three** Sections – **A**, **B** and **C**.
- (iii) **Section A** – Questions no. **1** to **3** are very short answer type questions, carrying **2** marks each.
- (iv) **Section B** – Questions no. **4** to **11** are short answer type questions, carrying **3** marks each.
- (v) **Section C** – Question no. **12** is case based question, carrying **5** marks.
- (vi) Use of log tables and calculators is **not** allowed.

Section A (6 marks)

1. Predict the products formed when $\text{CH}_3\text{CH}_2\text{CHO}$ reacts with the following reagents : (Any two)

(i) PhMgBr and then H_3O^+

(ii) LiAlH_4

(iii) HCN

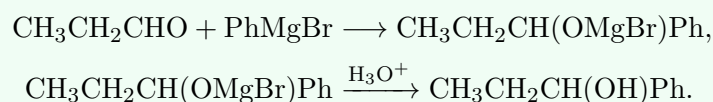
[2 marks]

Solution:

Concept:

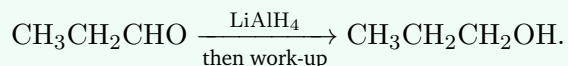
- Propanal, $\text{CH}_3\text{CH}_2\text{CHO}$, contains a polar carbonyl group; its carbonyl carbon is electrophilic and undergoes nucleophilic addition.
- A Grignard reagent adds a carbon group, LiAlH_4 reduces an aldehyde to a primary alcohol, and HCN adds across the carbonyl group to form a cyanohydrin.

Step 1: (i) Addition of phenylmagnesium bromide The phenyl group ($\text{Ph} = \text{C}_6\text{H}_5$) attacks the carbonyl carbon. The resulting magnesium alkoxide is protonated during the acidic work-up:



The original aldehydic hydrogen remains on the carbon bearing the hydroxyl group, giving a secondary alcohol.

Step 2: (ii) Reduction with lithium aluminium hydride Hydride adds to the carbonyl carbon; protonation of the resulting alkoxide on work-up gives the alcohol. The carbon skeleton remains unchanged:



Step 3: (iii) Addition of hydrogen cyanide Cyanide attacks the carbonyl carbon, and protonation of oxygen gives the cyanohydrin. The OH and CN groups are attached to the same carbon:



Step 4: Conclusion The products are (i) $\text{C}_6\text{H}_5\text{CH}(\text{OH})\text{CH}_2\text{CH}_3$, 1-phenylpropan-1-ol; (ii) $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$, propan-1-ol; and (iii) $\text{CH}_3\text{CH}_2\text{CH}(\text{OH})\text{CN}$, 2-hydroxybutanenitrile. Any two may be written as requested.

Quick Tip to Solve: Keep propanal's three-carbon chain intact: attach Ph or CN to its carbonyl carbon for addition, but convert CHO into CH_2OH for reduction.

2. Define molar conductivity for the solution of an electrolyte. How does it vary with concentration?

[2 marks]

Solution:

Concept:

- Molar conductivity, Λ_m , represents the conducting ability of all the ions supplied by one mole of an electrolyte in solution.
- $\Lambda_m = \kappa/c$ in consistent SI units, where κ is conductivity and c is molar concentration in mol m^{-3} .

Step 1: Define molar conductivity Molar conductivity is the conductance of the volume of solution containing one mole of an electrolyte, placed between two parallel electrodes of unit separation and an area large enough to contain the entire volume between them. If κ is expressed in S cm^{-1} and concentration C in mol L^{-1} , then

$$\Lambda_m = \frac{1000\kappa}{C},$$

with units $\text{S cm}^2 \text{mol}^{-1}$.

Step 2: Explain the concentration dependence On decreasing concentration (dilution), molar conductivity increases. For a strong electrolyte, dilution reduces interionic attractions and increases ionic mobility, so the increase is gradual. At low concentrations its variation is described by $\Lambda_m = \Lambda_m^\circ - A\sqrt{C}$, where Λ_m° is the limiting molar conductivity and A is a positive constant for the given electrolyte, solvent and temperature. For a weak electrolyte, dilution also greatly increases the degree of ionisation, producing a much sharper increase in molar conductivity.

Step 3: Conclusion Molar conductivity is the conductance associated with the solution containing one mole of electrolyte at unit electrode separation. It decreases as concentration increases, or equivalently increases on dilution, approaching Λ_m° at infinite dilution.

Quick Tip to Solve: Distinguish conductivity from molar conductivity: dilution lowers ions per unit volume but increases the conducting ability per mole of electrolyte.

3. In a reaction $2\text{N}_2\text{O}_5(\text{g}) \rightarrow 4\text{NO}_2(\text{g}) + \text{O}_2(\text{g})$, the concentration of N_2O_5 decreases from 0.5 mol L^{-1} to 0.4 mol L^{-1} in 10 minutes. Calculate the average rate of this reaction and rate of production of NO_2 during this period.

[2 marks]

Solution:

Concept:

- The average reaction rate is the change in concentration over a finite time interval, divided by the species' stoichiometric coefficient. A minus sign makes the rate positive for a disappearing reactant.
- For $2\text{N}_2\text{O}_5 \rightarrow 4\text{NO}_2 + \text{O}_2$,

$$r_{\text{av}} = -\frac{1}{2} \frac{\Delta[\text{N}_2\text{O}_5]}{\Delta t} = \frac{1}{4} \frac{\Delta[\text{NO}_2]}{\Delta t},$$

where square brackets denote molar concentrations and Δt is the time interval.

Step 1: Calculate the rate of disappearance of the reactant The concentration change is final minus

Quick Tip to Solve: Divide the N_2O_5 disappearance rate by 2 for the reaction rate, then multiply by 4 for NO_2 formation; do not equate all three rates.

initial:

$$\Delta[\text{N}_2\text{O}_5] = 0.4 - 0.5 = -0.1 \text{ mol L}^{-1}.$$

In the given 10 min, the average disappearance rate is

$$-\frac{\Delta[\text{N}_2\text{O}_5]}{\Delta t} = -\frac{-0.1}{10} = 0.010 \text{ mol L}^{-1} \text{ min}^{-1}.$$

Step 2: Apply the stoichiometric factors Divide the disappearance rate by the coefficient 2 to obtain the average rate of the reaction:

$$r_{\text{av}} = \frac{0.010}{2} = 0.0050 \text{ mol L}^{-1} \text{ min}^{-1}.$$

Four moles of NO_2 form per two moles of N_2O_5 consumed. Thus its formation rate is twice the disappearance rate, or four times the reaction rate:

$$\frac{\Delta[\text{NO}_2]}{\Delta t} = 4r_{\text{av}} = 4(0.0050) = 0.020 \text{ mol L}^{-1} \text{ min}^{-1}.$$

Step 3: Conclusion The average reaction rate is $5.0 \times 10^{-3} \text{ mol L}^{-1} \text{ min}^{-1}$, and the rate of production of NO_2 is $2.0 \times 10^{-2} \text{ mol L}^{-1} \text{ min}^{-1}$. In seconds these are 8.33×10^{-5} and $3.33 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$, respectively.

Quick Tip to Solve: Divide the N_2O_5 disappearance rate by 2 for the reaction rate, then multiply by 4 for NO_2 formation; do not equate all three rates.

Section B (24 marks)

4. Account for the following :

(i) Transition metals and their compounds show catalytic activities.

(ii) Zn, Cd and Hg are non-transition elements.

(iii) Zr and Hf are of almost identical atomic radii.

[3 marks]

Solution:

Concept:

- A transition element has an incompletely filled d subshell in its atom or in one of its common oxidation states. Membership of the d -block alone is insufficient.
- Transition-metal catalysis is associated with variable oxidation states and with adsorption or intermediate-complex formation, which provides a pathway of lower activation energy.
- Lanthanoid contraction is the gradual decrease in atomic and ionic size across the lanthanoids, caused by ineffective shielding by $4f$ electrons.

Step 1: (i) Relate catalysis to electronic structure Transition metals can use different oxidation states because their $(n-1)d$ and ns orbital energies are comparable. They can therefore accept and donate electrons during a reaction and form temporary intermediates with reactants. The catalyst

Quick Tip to Solve: For these three reasons, check oxidation-state flexibility, then d -subshell occupancy, then whether a $5d$ element follows the lanthanoids.

is regenerated at the end of the cycle. In heterogeneous catalysis, adsorption on the metal surface brings reactants together and weakens their bonds. These effects lower the activation energy and increase the reaction rate.

Step 2: (ii) Examine the occupied d subshells The atoms of Zn, Cd and Hg have configurations $(n-1)d^{10}ns^2$. Removal of the two outer s electrons gives their usual divalent ions, Zn^{2+} , Cd^{2+} and Hg^{2+} , each with a completely filled d^{10} subshell. Thus neither their atoms nor their common ions have a partially filled d subshell, so they do not satisfy the definition of transition elements.

Step 3: (iii) Apply lanthanoid contraction Hf follows the lanthanoid series, whereas Zr lies in the preceding transition series. Across the lanthanoids, electrons enter the $4f$ subshell and shield the increasing nuclear charge poorly. The increased effective nuclear attraction contracts the electron cloud. This contraction almost offsets the size increase expected from the extra shell in Hf; consequently, Zr and Hf have nearly identical atomic radii.

Step 4: Conclusion (i) Variable oxidation states, intermediate formation and surface adsorption explain catalytic activity. (ii) Filled d^{10} subshells make Zn, Cd and Hg non-transition elements. (iii) Lanthanoid contraction makes the radii of Zr and Hf almost identical.

Quick Tip to Solve: For these three reasons, check oxidation-state flexibility, then d-subshell occupancy, then whether a 5d element follows the lanthanoids.

5. From the given $E^\ominus$ values of the first row transition elements, answer the following questions :

(i) Why is $E^\ominus_{Mn^{2+}/Mn}$ value highly negative as compared to other elements?

(ii) What is the reason for the irregularity in the above $E^\ominus$ values?

(iii) Why is $E^\ominus_{Cu^{2+}/Cu}$ value exceptionally positive?

[3 marks]

$E^\ominus_{M^{2+}/M}$	Cr	Mn	Fe	Co	Ni	Cu	Zn
	-0.91	-1.18	-0.44	-0.28	-0.25	+0.34	-0.76

Solution:

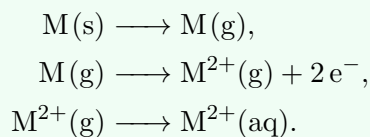
Concept:

- The tabulated $E^\ominus_{M^{2+}/M}$ is the standard reduction potential for $M^{2+}(aq) + 2e^- \longrightarrow M(s)$. A more negative value indicates less favourable reduction relative to the standard hydrogen electrode.
- Formation of $M^{2+}(aq)$ from the metal involves atomisation, the first two ionisations, and hydration. Their combined energetic effect helps explain the electrode-potential trends.
- Half-filled d^5 and completely filled d^{10} configurations have extra stability; their formation or disruption affects ionisation energies and the stability of metal ions.

Step 1: (i) Identify the stable manganese ion The electronic configuration of Mn is $[Ar]3d^54s^2$. Losing its two $4s$ electrons produces Mn^{2+} , with the particularly stable half-filled $3d^5$ configuration. This stabilises the divalent state and makes its reduction back to the metal relatively difficult. Hence the reduction potential $E^\ominus_{Mn^{2+}/Mn} = -1.18V$ is highly negative.

Quick Tip to Solve: Read the potential as a reduction: stabilising the aqueous divalent ion makes reduction harder. For copper, compare the cost of atomisation and ionisation with the hydration energy released.

Step 2: (ii) Compare the competing energy changes The metal-to-aqueous-ion conversion can be separated into the following stages:



Atomisation and ionisation require energy, whereas hydration releases energy. Atomisation enthalpy and the sum of the first two ionisation enthalpies vary irregularly across the series, partly because d-electron configurations change. Hydration enthalpy also contributes. Their combined effect therefore does not vary smoothly, so neither do the standard electrode potentials; no single one of these factors determines the trend alone.

Step 3: (iii) Account for the positive copper value Copper has a high energy requirement for atomisation and ionisation. In particular, removal of the second electron disrupts the stable $3d^{10}$ configuration of Cu^+ . The energy released on hydrating Cu^{2+} is insufficient to compensate for the high atomisation and ionisation energies. Consequently, oxidation of copper to aqueous Cu^{2+} is relatively unfavourable, and its standard reduction potential is positive: $E^\circ_{\text{Cu}^{2+}/\text{Cu}} = +0.34\text{ V}$.

Step 4: Conclusion (i) The stable half-filled $3d^5$ configuration of Mn^{2+} explains the highly negative manganese value. (ii) Competing atomisation, ionisation and hydration contributions explain the irregularity. (iii) Copper's high atomisation and ionisation energies are not compensated by hydration, giving the exceptionally positive value.

Quick Tip to Solve: Read the potential as a reduction: stabilising the aqueous divalent ion makes reduction harder. For copper, compare the cost of atomisation and ionisation with the hydration energy released.

6(a). Write three differences between Lyophobic sol and Lyophilic sol.

[3 marks]

Solution:

Concept:

- A sol consists of colloidal particles dispersed in a liquid. Lyophilic means solvent-loving, whereas lyophobic means solvent-hating.
- The affinity of particles for the dispersion medium determines their solvation, ease of preparation and reversibility.

Step 1: Compare affinity for the dispersion medium In a lyophobic sol, the dispersed particles have little or no affinity for the dispersion medium and are not appreciably solvated. In a lyophilic sol, the particles have a strong affinity for the medium and become extensively solvated. The surrounding solvent layer helps keep lyophilic particles dispersed.

Step 2: Compare the method of preparation A lyophobic sol cannot generally be prepared merely by mixing the substance with the dispersion medium; special dispersion or condensation methods are needed. A lyophilic sol is readily formed by bringing the substance into contact with a suitable dispersion medium, sometimes with warming. For example, starch forms a lyophilic sol in hot water,

Quick Tip to Solve: Compare both sols on the same three bases: affinity, preparation and reversibility. Associate solvent-loving particles with easy sol formation and reversibility.

whereas a gold sol requires a special preparation method.

Step 3: Compare reversibility Lyophobic sols are irreversible: after the dispersed phase separates by coagulation, simply adding the dispersion medium does not restore the sol. Lyophilic sols are reversible: after removal of the medium, the sol can generally be formed again by adding the medium under suitable conditions. This difference follows from the strong particle–solvent affinity in lyophilic sols.

Step 4: Conclusion The three differences are affinity (little in lyophobic, strong in lyophilic), preparation (special methods versus direct contact with a suitable solvent), and reversibility (irreversible versus reversible).

Quick Tip to Solve: Compare both sols on the same three bases: affinity, preparation and reversibility. Associate solvent-loving particles with easy sol formation and reversibility.

OR

6(b). (i) Write the dispersed phase and dispersion medium of ‘milk’.

(ii) What is the cause of Brownian movement in colloidal particles?

(iii) Why does physisorption decrease with increase in temperature?

[3 marks]

Solution:

Concept:

- An emulsion contains one liquid dispersed as fine droplets in another liquid. Its dispersed phase is the droplet material and its dispersion medium is the continuous liquid.
- Brownian movement is the irregular, zigzag motion of colloidal particles caused by collisions with molecules of the dispersion medium.
- Physisorption is exothermic. Increasing temperature favours the reverse process, desorption, according to Le Chatelier’s principle.

Step 1: Identify the two phases of milk (i) Milk is an oil-in-water emulsion. Small droplets of liquid fat are distributed throughout an aqueous continuous phase. Therefore, its dispersed phase is liquid fat (oil), and its dispersion medium is water. The fat droplets are the discontinuous phase; water surrounds and carries them.

Step 2: Explain the irregular motion of colloidal particles (ii) Molecules of the dispersion medium are in continuous thermal motion and strike each colloidal particle from different directions. At any instant the impacts on different sides are unequal, producing an unbalanced impulse. Successive impulses vary randomly in direction and magnitude, so the colloidal particle follows an irregular zigzag path. These unequal molecular collisions cause Brownian movement.

Step 3: Apply the temperature effect to physisorption (iii) In physisorption, weak van der Waals attractions bind adsorbate particles to the surface and heat is released. Thus the adsorption enthalpy satisfies $\Delta H < 0$. Raising the temperature shifts the adsorption–desorption equilibrium towards desorption, which absorbs heat. Consequently, at a given pressure, fewer adsorbate particles remain on the surface and the extent of physisorption decreases.

Quick Tip to Solve: For milk, remember oil-in-water: the first liquid is dispersed. For temperature effects, use the sign of adsorption enthalpy before applying Le Chatelier’s principle.

Step 4: Conclusion Milk has liquid fat as its dispersed phase and water as its dispersion medium. Brownian movement results from unequal collisions by medium molecules. Physisorption decreases on heating because adsorption is exothermic and higher temperature favours desorption.

Quick Tip to Solve: For milk, remember oil-in-water: the first liquid is dispersed. For temperature effects, use the sign of adsorption enthalpy before applying Le Chatelier's principle.

7(a). Write the equations involved in the following reactions :

(i) Cannizzaro reaction

(ii) Aldol condensation

(iii) Hell-Volhard-Zelinsky reaction

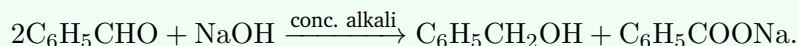
[3 marks]

Solution:

Concept:

- Cannizzaro reaction is the disproportionation of an aldehyde without an α -hydrogen in concentrated alkali: one molecule is oxidised and another is reduced.
- Aldehydes or ketones containing an α -hydrogen undergo aldol addition in dilute alkali; heating the product causes dehydration to an α, β -unsaturated carbonyl compound.
- Hell-Volhard-Zelinsky (HVZ) reaction replaces an α -hydrogen of a carboxylic acid by chlorine or bromine in the presence of red phosphorus.

Step 1: (i) Cannizzaro reaction Benzaldehyde has no α -hydrogen and reacts with concentrated aqueous sodium hydroxide as follows:

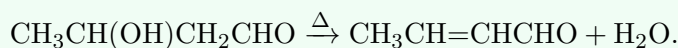


The products are benzyl alcohol and sodium benzoate. The salt, rather than free benzoic acid, is written because the reaction mixture is alkaline.

Step 2: (ii) Aldol condensation Ethanal contains α -hydrogens. Two molecules first form the aldol, 3-hydroxybutanal, in dilute sodium hydroxide:

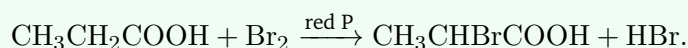


On heating, the aldol loses water to give but-2-enal (crotonaldehyde):



Including the dehydration step distinguishes aldol condensation from aldol addition alone.

Step 3: (iii) Hell-Volhard-Zelinsky reaction Propanoic acid undergoes bromination at the carbon adjacent to its carboxyl group:



Quick Tip to Solve: Check for an α -hydrogen first: its absence selects Cannizzaro, while its presence enables aldol reaction or α -halogenation of a carboxylic acid.

This net equation, with hydrolysis during work-up, gives 2-bromopropanoic acid. Bromine replaces an α -hydrogen; it does not replace the hydrogen of the carboxyl group.

Step 4: Conclusion Cannizzaro gives an alcohol and a carboxylate salt; aldol condensation gives an α, β -unsaturated aldehyde and water; HVZ gives an α -halocarboxylic acid, as shown in the equations above.

Quick Tip to Solve: Check for an α -hydrogen first: its absence selects Cannizzaro, while its presence enables aldol reaction or α -halogenation of a carboxylic acid.

OR

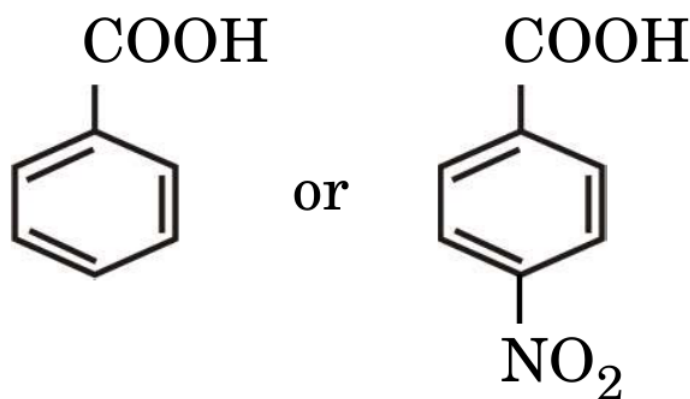
7(b). (i) Which acid of each pair would you expect to be stronger? Give reason.

(I) $\text{F}-\text{CH}_2-\text{COOH}$ or $\text{Cl}-\text{CH}_2-\text{COOH}$

(II)

(ii) Distinguish between Propanal and Propanone.

[3 marks]



Solution:

Concept:

- For $\text{RCOOH} \rightleftharpoons \text{RCOO}^- + \text{H}^+$, electron-withdrawing substituents stabilise the carboxylate ion, favour ionisation and increase acid strength.
- Tollens' reagent, an alkaline solution of $[\text{Ag}(\text{NH}_3)_2]^+$, oxidises aldehydes while silver(I) is reduced to metallic silver. Ordinary ketones do not give this test.

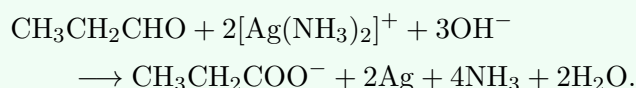
Step 1: (i)(I) Compare the haloacetic acids Fluorine is more electronegative than chlorine and has a stronger electron-withdrawing inductive ($-I$) effect. At the same distance from COOH , fluorine therefore stabilises FCH_2COO^- more strongly than chlorine stabilises $\text{ClCH}_2\text{COO}^-$, favouring proton loss from fluoroacetic acid.

Step 2: (i)(II) Compare the aromatic acids The printed pair is benzoic acid and *p*-nitrobenzoic acid. The para NO_2 group withdraws electron density by its $-I$ and $-R$ effects. It stabilises the conjugate base relative to benzoate, so *p*-nitrobenzoic acid ionises more readily.

Step 3: (ii) Apply Tollens' test Add freshly prepared Tollens' reagent separately to the samples and

Quick Tip to Solve: Stronger electron withdrawal increases carboxylic acid strength; a silver mirror identifies the aldehyde in this pair.

warm gently in a water bath. Propanal gives a silver mirror (or metallic silver deposit); propanone gives no silver mirror. Propanal is oxidised to propanoate in the alkaline medium:



Propanone resists oxidation under these mild conditions.

Step 4: Conclusion (i)(I) FCH_2COOH is stronger than ClCH_2COOH ; (i)(II) *p*-nitrobenzoic acid is stronger than benzoic acid. (ii) Propanal gives a positive Tollens' test; propanone does not.

Quick Tip to Solve: Stronger electron withdrawal increases carboxylic acid strength; a silver mirror identifies the aldehyde in this pair.

8. A first order reduction takes 30 minutes for 75% decomposition. Calculate $t_{1/2}$.

Given : [$\log 2 = 0.3$, $\log 3 = 0.48$, $\log 4 = 0.6$, $\log 5 = 0.7$]

[3 marks]

Solution:

Concept:

- For a first order reaction, $k = \frac{2.303}{t} \log \frac{[A]_0}{[A]_t}$, where k is the rate constant and $[A]_0$ and $[A]_t$ are the initial and remaining reactant concentrations.
- The half-life is $t_{1/2} = \frac{2.303 \log 2}{k}$. It is independent of the initial concentration, so successive halvings take equal times.

Step 1: Find the fraction of reactant remaining After 30 minutes, 75% has decomposed. The concentration used in the first order equation is the amount remaining, not the amount decomposed. Hence,

$$[A]_{30} = \frac{100 - 75}{100} [A]_0 = \frac{[A]_0}{4}, \quad \frac{[A]_0}{[A]_{30}} = 4.$$

Step 2: Calculate the rate constant Substitute the concentration ratio and the given value $\log 4 = 0.6$:

$$k = \frac{2.303}{30} \log 4 = \frac{2.303 \times 0.6}{30} = 0.04606 \text{ min}^{-1}.$$

Since the time was taken in minutes, the rate constant has units of reciprocal minutes.

Step 3: Use the half-life relation With the supplied value $\log 2 = 0.3$,

$$t_{1/2} = \frac{2.303 \times 0.3}{0.04606} = 15 \text{ min}.$$

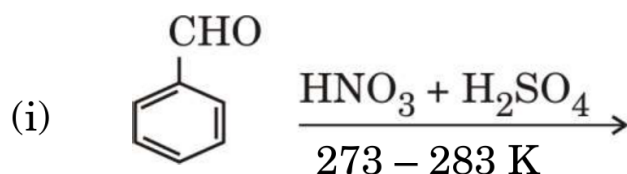
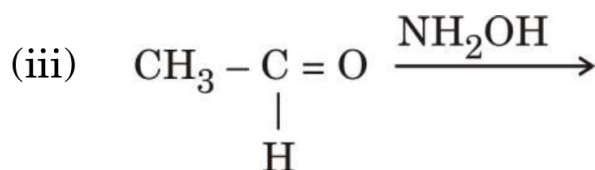
This also follows directly from the remaining fraction: the first half-life leaves one-half of the original reactant, and the second leaves one-quarter. Thus, 75% decomposition represents exactly two half-lives in 30 minutes.

Step 4: Conclusion The half-life of the first order reduction is $t_{1/2} = 15 \text{ min}$.

Quick Tip to Solve: For a first order process, 75% decomposition leaves 25%, or one-quarter: count two equal half-lives and divide the elapsed time by two.

9(a). Write the major products in the following :

[3 marks]



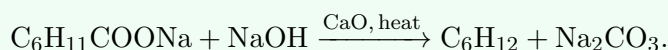
Solution:

Concept:

- The aldehyde group, $-\text{CHO}$, withdraws electrons from a benzene ring and directs electrophilic substitution mainly to the meta position.
- Soda lime removes the carboxyl carbon of a sodium carboxylate: $\text{RCOONa} + \text{NaOH} \longrightarrow \text{RH} + \text{Na}_2\text{CO}_3$, where R is the attached hydrocarbon group.
- Carbonyl compounds condense with hydroxylamine, NH_2OH , to form oximes, replacing $\text{C}=\text{O}$ by $\text{C}=\text{N}-\text{OH}$ with loss of water.

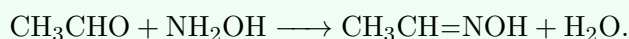
Step 1: Identify the nitration product in (i) The starting compound is benzaldehyde. The $\text{HNO}_3-\text{H}_2\text{SO}_4$ mixture nitrates its ring. Since $-\text{CHO}$ is meta-directing, the incoming $-\text{NO}_2$ group replaces a ring hydrogen mainly at position 3, giving 3-nitrobenzaldehyde, $3-\text{NO}_2-\text{C}_6\text{H}_4-\text{CHO}$.

Step 2: Decarboxylate the salt in (ii) The ring is saturated: the reactant is sodium cyclohexanecarboxylate. Heating with soda lime replaces $-\text{COONa}$ by hydrogen while preserving the six-membered ring:



The organic product is cyclohexane; the carboxyl carbon becomes part of the carbonate.

Step 3: Form the oxime in (iii) The carbonyl carbon has a methyl group and hydrogen, so the aldehyde is ethanal. Condensation with hydroxylamine gives ethanal oxime (acetaldoxime):



Step 4: Conclusion The major products are (i) 3-nitrobenzaldehyde; (ii) cyclohexane; and (iii) ethanal oxime.

Quick Tip to Solve: Read the ring bonds first: soda lime removes the carboxyl carbon, so the saturated six-membered ring in (ii) gives cyclohexane.

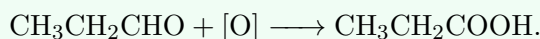
- 9(b). (i) Oxidation of propanal is easier than propanone. Why?
 (ii) How can you distinguish between Acetophenone and Benzophenone?
 (iii) Draw the structure of the following derivative : 2,4-Dinitrophenylhydrazone of Propanone.

[3 marks]

Solution:**Concept:**

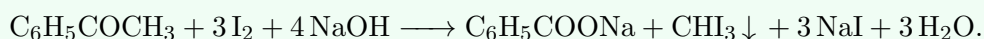
- Aldehydes oxidise readily to carboxylic acids; ketone oxidation requires carbon-carbon bond cleavage and stronger conditions.
- Methyl ketones, RCOCH_3 , give yellow iodoform, CHI_3 , with iodine and aqueous alkali.
- Hydrazone formation replaces carbonyl oxygen by $=\text{N}-\text{NH}-\text{Ar}$; here Ar is the 2,4-dinitrophenyl group.

Step 1: (i) Compare oxidation of propanal and propanone Propanal, $\text{CH}_3\text{CH}_2\text{CHO}$, has a hydrogen on its carbonyl carbon. It is readily oxidised to propanoic acid without breaking the carbon skeleton:



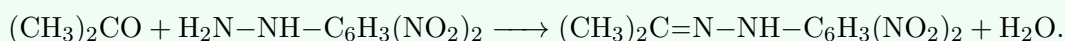
Propanone, CH_3COCH_3 , lacks this hydrogen. Its oxidation requires carbon-carbon bond cleavage, so it resists mild oxidants and is harder to oxidise.

Step 2: (ii) Apply the iodoform test Warm each compound separately with iodine and aqueous sodium hydroxide. Acetophenone, $\text{C}_6\text{H}_5\text{COCH}_3$, contains a methyl ketone group and gives a yellow precipitate of iodoform:



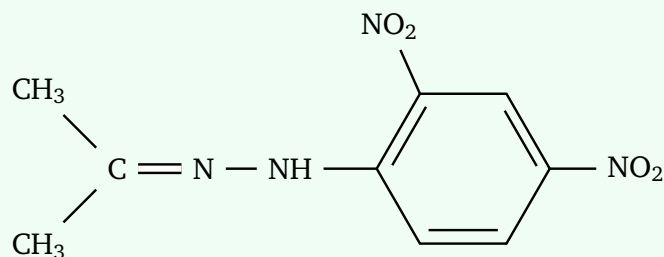
Benzophenone, $\text{C}_6\text{H}_5\text{COC}_6\text{H}_5$, has no CH_3CO^- group, so it gives no yellow iodoform precipitate. This difference distinguishes the two ketones.

Step 3: (iii) Form the propanone derivative Condense propanone with 2,4-dinitrophenylhydrazine, eliminating water:



Both methyl groups remain on the carbon of $\text{C}=\text{N}$; the nitro groups are ortho and para to the ring's $-\text{NH}-$ attachment.

Quick Tip to Solve: Look for CH_3CO^- to predict iodoform formation. In the hydrazone, retain both methyl groups on the carbon of $\text{C}=\text{N}$.



2,4-Dinitrophenylhydrazone of propanone

Step 4: Conclusion Propanal oxidises readily without carbon-carbon bond cleavage. Acetophenone gives yellow CHI_3 , whereas benzophenone does not. The required derivative is $(\text{CH}_3)_2\text{C}=\text{N}-\text{NH}-\text{C}_6\text{H}_3(\text{NO}_2)_2$, with nitro groups at positions 2 and 4.

Quick Tip to Solve: Look for CH_3CO^- to predict iodoform formation. In the hydrazone, retain both methyl groups on the carbon of $\text{C}=\text{N}$.

10. Calculate the emf of the following cell :



Given : $E_{\text{Zn}^{2+}/\text{Zn}}^\circ = -0.76 \text{ V}$ and $E_{\text{Ag}^+/\text{Ag}}^\circ = +0.80 \text{ V}$

[log 2 = 0.3010, log 3 = 0.4771, log 10 = 1]

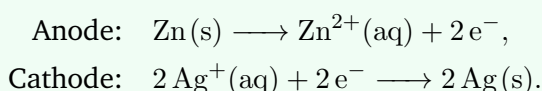
[3 marks]

Solution:

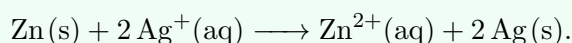
Concept:

- For a galvanic cell, $E_{\text{cell}}^\circ = E_{\text{cathode}}^\circ - E_{\text{anode}}^\circ$, using standard reduction potentials for both electrodes.
- At 298 K, the Nernst equation is $E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{0.0591}{n} \log Q$, where n is the number of electrons transferred and Q is the reaction quotient. Pure solids have unit activity.

Step 1: Write the balanced cell reaction Zinc is oxidised at the left electrode (anode), and silver ions are reduced at the right electrode (cathode):



Adding the half-reactions gives



Thus $n = 2$. The coefficient of silver ions will also appear as a power in the reaction quotient.

Step 2: Calculate the standard cell potential The given values are reduction potentials. Subtract the zinc reduction potential from the silver reduction potential:

$$E_{\text{cell}}^\circ = 0.80 - (-0.76) = 1.56 \text{ V}.$$

Electrode potentials are not multiplied by the coefficients used to balance the half-reactions.

Quick Tip to Solve: Balance the electron transfer first: two silver ions are needed per zinc atom, so use both $n = 2$ and the square of the silver-ion concentration in Q .

Step 3: Calculate the concentration correction Taking concentrations relative to the standard concentration, and omitting the pure solids, the reaction quotient is

$$Q = \frac{[\text{Zn}^{2+}]}{[\text{Ag}^+]^2} = \frac{0.01}{(0.001)^2} = 10^4.$$

Hence $\log Q = 4 \log 10 = 4$. Using the usual room-temperature Nernst equation at 298 K,

$$\begin{aligned} E_{\text{cell}} &= 1.56 - \frac{0.0591}{2} \times 4 \\ &= 1.56 - 0.1182 \\ &= 1.4418 \text{ V.} \end{aligned}$$

Since $Q > 1$, the correction lowers the emf below its standard value, providing a check on the sign.

Step 4: Conclusion The emf of the cell at 298 K is $E_{\text{cell}} \approx 1.44 \text{ V}$.

Quick Tip to Solve: Balance the electron transfer first: two silver ions are needed per zinc atom, so use both $n = 2$ and the square of the silver-ion concentration in Q .

11(a). Write the hybridisation and magnetic character of the following complexes :

(i) $[\text{NiCl}_4]^{2-}$

(ii) $[\text{Co}(\text{NH}_3)_6]^{3+}$

(iii) $[\text{FeF}_6]^{3-}$

[Atomic number : Ni = 28, Co = 27, Fe = 26]

[3 marks]

Solution:

Concept:

- Find the oxidation state and then the metal ion's d -electron count. Electrons are removed from the $4s$ orbital before the $3d$ orbitals when a first-row transition metal forms a cation.
- In valence bond theory, a tetrahedral complex uses sp^3 hybridisation. An octahedral complex uses either inner-orbital d^2sp^3 or outer-orbital sp^3d^2 hybridisation, depending on electron pairing.
- Unpaired electrons cause paramagnetism; a complex with all electrons paired is diamagnetic. Ligand strength and the metal ion together determine whether pairing occurs.

Step 1: Analyse the nickel complex In $[\text{NiCl}_4]^{2-}$, let the oxidation state of nickel be x . Then $x - 4 = -2$, giving $x = +2$. Neutral nickel is $[\text{Ar}] 3d^8 4s^2$, so Ni^{2+} is $3d^8$. The weak-field Cl^- ligands produce a tetrahedral complex. One $4s$ and three $4p$ orbitals form four sp^3 hybrid orbitals. The $3d^8$ configuration has two unpaired electrons, so the complex is paramagnetic.

Step 2: Analyse the cobalt complex In $[\text{Co}(\text{NH}_3)_6]^{3+}$, all six ammonia ligands are neutral, so cobalt has oxidation state +3. Neutral cobalt is $[\text{Ar}] 3d^7 4s^2$; hence Co^{3+} is $3d^6$. For this cobalt(III) complex, ammonia causes the six $3d$ electrons to pair in three orbitals, leaving two $3d$ orbitals vacant. These two orbitals, one $4s$ and three $4p$ orbitals give d^2sp^3 hybridisation. The octahedral complex has no unpaired electrons and is diamagnetic.

Quick Tip to Solve: Determine the metal oxidation state before counting d electrons: the relevant counts here are d^8 , d^6 and d^5 , respectively.

Step 3: Analyse the iron complex In $[\text{FeF}_6]^{3-}$, $x - 6 = -3$, so iron is Fe^{3+} . Neutral iron is $[\text{Ar}] 3d^6 4s^2$, and Fe^{3+} is therefore $3d^5$. Fluoride is a weak-field ligand and does not pair these five $3d$ electrons. The six coordinate bonds use one $4s$, three $4p$ and two outer $4d$ orbitals, giving sp^3d^2 hybridisation. Five unpaired electrons make this octahedral complex paramagnetic.

Step 4: Conclusion (i) $[\text{NiCl}_4]^{2-}$: sp^3 , paramagnetic (two unpaired electrons).

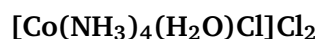
(ii) $[\text{Co}(\text{NH}_3)_6]^{3+}$: $d^2 sp^3$, diamagnetic.

(iii) $[\text{FeF}_6]^{3-}$: sp^3d^2 , paramagnetic (five unpaired electrons).

Quick Tip to Solve: Determine the metal oxidation state before counting d electrons: the relevant counts here are d^8 , d^6 and d^5 , respectively.

OR

11(b). (i) Write the IUPAC name of the following complex :



(ii) What is the difference between an Ambidentate ligand and a Bidentate ligand?

(iii) Out of $[\text{Fe}(\text{NH}_3)_6]^{3+}$ and $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$, which complex is more stable and why?

[3 marks]

Solution:

Concept:

- In coordination nomenclature, name ligands alphabetically, ignoring multiplicative prefixes, then the metal with its oxidation state in Roman numerals. Name the cation before the anion.
- Denticity counts the donor atoms of one ligand that bind simultaneously to the same metal ion. An ambidentate ligand has alternative donor atoms but uses only one in a given mode of attachment.
- A multidentate ligand forms a chelate ring when two or more donor atoms bind to the same metal. Chelation generally increases the stability of a complex relative to a comparable complex with monodentate ligands.

Step 1: Name the cobalt coordination compound In $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})\text{Cl}]\text{Cl}_2$, the two chloride counterions show that the complex cation has charge +2. Ammonia and water are neutral, while the coordinated chloride has charge -1. Thus the cobalt oxidation state satisfies $x - 1 = +2$, giving $x = +3$. The ligand names in alphabetical order are ammine, aqua and chlorido; the four ammine ligands require the prefix tetra. Since the coordination entity is a cation, the metal name stays cobalt. The complete name is tetraammineaquachloridocobalt(III) chloride.

Step 2: Distinguish the two ligand types An ambidentate ligand can attach through either of two different donor atoms, but only one donor atom binds to a given metal at a time. For example, NO_2^- can bind through nitrogen or oxygen. A bidentate ligand attaches through two donor atoms simultaneously to the same metal, usually forming a ring. For example, ethane-1,2-diamine binds through both nitrogen atoms; oxalate, $\text{C}_2\text{O}_4^{2-}$, binds through two oxygen atoms. Thus having alternative attachment sites is different from using two sites together.

Step 3: Compare the stability of the iron complexes Both complexes contain Fe^{3+} with coordination number six. In $[\text{Fe}(\text{NH}_3)_6]^{3+}$, each ammonia ligand is monodentate and no chelate rings form. In

Quick Tip to Solve: For the name, use the two external chlorides to find cobalt's oxidation state. For stability, count chelate rings rather than just donor atoms.

$[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$, each of the three oxalate ligands is bidentate and forms a chelate ring with iron. This multiple-point attachment produces the chelate effect, increasing the stability of the oxalate complex. Coordination number alone therefore does not determine which complex is more stable.

Step 4: Conclusion (i) Tetraammineaquachloridocobalt(III) chloride.

(ii) An ambidentate ligand binds through one of its alternative donor atoms; a bidentate ligand binds through two donor atoms simultaneously.

(iii) $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$ is more stable owing to the chelate effect of bidentate oxalate ligands.

Quick Tip to Solve: For the name, use the two external chlorides to find cobalt's oxidation state. For stability, count chelate rings rather than just donor atoms.

Section C (5 marks)

12(i). Read the following passage and answer the questions that follow :

Amines constitute an important class of organic compounds derived by replacing one or more hydrogen atoms of ammonia molecule by alkyl/aryl groups. Amines are usually formed from nitro compounds, halides, amides, etc. They exhibit hydrogen bonding which influences their physical properties. Alkyl amines are found to be stronger bases than ammonia. In aromatic amines, electron releasing and withdrawing groups, respectively increase and decrease their basic character. Reactions of amines are governed by availability of the unshared pair of electrons on nitrogen. Influence of the number of hydrogen atoms at nitrogen atom on the type of reactions and nature of products is responsible for identification and distinction between primary, secondary and tertiary amines. Reactivity of aromatic amines can be controlled by acylation process.

Why does aniline not give Friedel-Crafts reaction?

[1 mark]

Solution:

Concept:

- Friedel–Crafts alkylation and acylation require a Lewis acid catalyst such as anhydrous AlCl_3 to generate the electrophile.
- Aniline is a Lewis base: its nitrogen lone pair can coordinate to an electron-deficient Lewis acid.

Step 1: Consider the interaction with the catalyst The lone pair on the nitrogen atom of aniline is donated to AlCl_3 , forming a Lewis acid–base complex. Consequently, the amino group cannot donate its lone pair to the benzene ring as it does in free aniline.

Step 2: Explain the effect on the ring Nitrogen acquires positive character in the complex. The complexed group withdraws electron density from the ring and strongly deactivates it towards electrophilic aromatic substitution under Friedel–Crafts conditions.

Step 3: Conclusion Aniline does not give the Friedel–Crafts reaction because it forms a complex with AlCl_3 ; the resulting deactivation prevents the required ring substitution.

Quick Tip to Solve: Before applying the activating effect of NH_2 , check whether the Lewis acid catalyst binds the nitrogen lone pair.

12(ii). Arrange the following in the increasing order of their pK_b values :

$C_6H_5NH_2$, NH_3 , $C_2H_5NH_2$, $(CH_3)_3N$

[1 mark]

Solution:

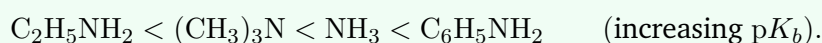
Concept:

- Base strength increases with K_b , while $pK_b = -\log K_b$; hence a stronger base has a smaller pK_b .
- In aqueous solution, the availability of the nitrogen lone pair and the hydration of the conjugate acid together determine amine basicity.

Step 1: Compare the aliphatic bases Alkyl groups release electron density towards nitrogen. In water, ethylamine, $C_2H_5NH_2$, is stronger than trimethylamine, $(CH_3)_3N$, because the combined inductive and solvation effects favour ethylamine. Both are stronger bases than NH_3 .

Step 2: Place aniline and reverse the order In aniline, $C_6H_5NH_2$, the nitrogen lone pair is delocalised into the benzene ring and is less available to accept a proton. Aniline is therefore the weakest base listed and has the largest pK_b . Reverse the basic-strength order to obtain increasing pK_b .

Step 3: Conclusion The increasing order is



Quick Tip to Solve: First rank aqueous basicity, then reverse it for pK_b ; aniline belongs at the high- pK_b end.

12(iii). How can you distinguish between $CH_3CH_2NH_2$ and $(CH_3CH_2)_2NH$ by Hinsberg test? [1 mark]

Solution:

Concept:

- Hinsberg reagent is benzenesulphonyl chloride, $C_6H_5SO_2Cl$. It reacts with primary and secondary amines to give sulphonamides.
- A primary amine's sulphonamide retains an acidic N-H hydrogen and dissolves in alkali; a secondary amine's product has no such hydrogen.

Step 1: Test ethylamine Shake $CH_3CH_2NH_2$ with Hinsberg reagent and aqueous KOH. The product $C_6H_5SO_2NHCH_2CH_3$ contains an acidic N-H bond and dissolves in excess alkali by forming its salt. Acidification regenerates the insoluble sulphonamide as a precipitate.

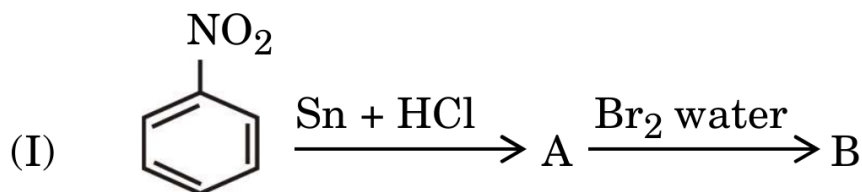
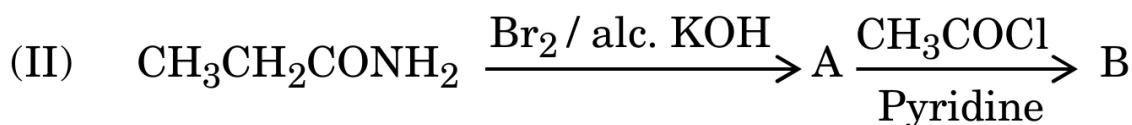
Step 2: Test diethylamine Under the same conditions, $(CH_3CH_2)_2NH$ gives $C_6H_5SO_2N(CH_2CH_3)_2$. This product has no hydrogen attached to nitrogen, cannot form the corresponding salt, and remains insoluble in aqueous alkali.

Step 3: Conclusion Ethylamine gives a sulphonamide soluble in alkali and precipitated on acidification; diethylamine gives a sulphonamide insoluble in alkali.

Quick Tip to Solve: Count the hydrogens on nitrogen after sulphonylation: one remaining N-H makes the primary-amine product alkali-soluble.

12(iv)(a). Write the structures of A and B in the following reactions :

[2 marks]

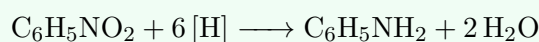


Solution:

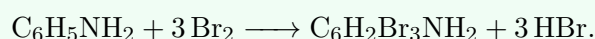
Concept:

- Reduction of an aromatic nitro group with Sn/HCl gives the corresponding amino group. Aniline strongly activates the ortho and para positions towards bromination.
- Hofmann bromamide degradation converts RCONH_2 into RNH_2 , removing the carbonyl carbon. Acetyl chloride then acylates an amine at nitrogen.

Step 1: Identify both products in reaction (I) The nitro group of nitrobenzene is reduced to an amino group, so A is aniline, $\text{C}_6\text{H}_5\text{NH}_2$ (the free amine obtained after work-up).

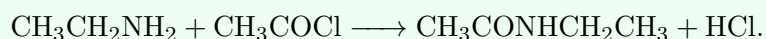


Bromine water substitutes at both ortho positions and the para position of the activated ring, producing white 2,4,6-tribromoaniline:



Thus B has NH_2 at carbon 1 and Br at carbons 2, 4 and 6.

Step 2: Identify both products in reaction (II) Propanamide, $\text{CH}_3\text{CH}_2\text{CONH}_2$, loses its carbonyl carbon in Hofmann degradation and gives A as ethylamine, $\text{CH}_3\text{CH}_2\text{NH}_2$. The two-carbon ethyl group remains attached to nitrogen. Reaction with acetyl chloride in pyridine replaces one nitrogen hydrogen by an acetyl group:



Pyridine takes up the acid formed. B is *N*-ethylacetamide. Its connectivity is:



Step 3: Conclusion (I) A: $\text{C}_6\text{H}_5\text{NH}_2$; B: 2,4,6- $\text{Br}_3\text{C}_6\text{H}_2\text{NH}_2$ (2,4,6-tribromoaniline).

(II) A: $\text{CH}_3\text{CH}_2\text{NH}_2$; B: $\text{CH}_3 - \text{C}(=\text{O}) - \text{NH} - \text{CH}_2 - \text{CH}_3$ (*N*-ethylacetamide).

Quick Tip to Solve: For (I), bromine water gives all three activated ring substitutions. For (II), remove the amide carbonyl carbon before adding the acetyl group to nitrogen.

12(iv)(b). How will you convert the following :

(I) Benzoic acid to aniline

(II) Aniline to *p*-bromoaniline

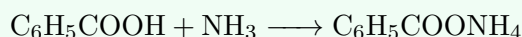
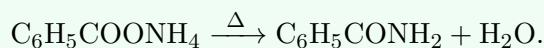
[2 marks]

Solution:

Concept:

- Hofmann bromamide degradation changes RCONH_2 into RNH_2 with loss of the carbonyl carbon. Thus benzamide is the suitable precursor to aniline.
- Acetylation protects the strongly activating amino group. Bromination of acetanilide gives mainly the para product, and hydrolysis then restores NH_2 .

Step 1: Convert benzoic acid into aniline Treat benzoic acid with ammonia to form ammonium benzoate, then heat the salt to obtain benzamide:

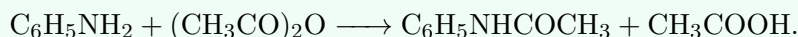


Heat benzamide with bromine and aqueous potassium hydroxide for Hofmann degradation:

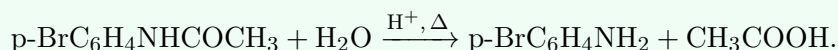


The carbon of the carboxyl group is removed, leaving an amino group directly attached to the benzene ring.

Step 2: Convert aniline into para-bromoaniline First acetylate aniline using acetic anhydride to form acetanilide:



Treat acetanilide with bromine in glacial acetic acid. The protected group directs substitution mainly to the para position, giving *p*-bromoacetanilide; isolate this major product. Heat it with aqueous acid to hydrolyse the acetyl group, then neutralise to liberate *p*-bromoaniline:



This last equation represents the net hydrolysis after work-up. Direct bromination of unprotected aniline with bromine water would instead produce 2,4,6-tribromoaniline.

Step 3: Conclusion (I) Benzoic acid $\longrightarrow$ ammonium benzoate $\longrightarrow$ benzamide $\longrightarrow$ aniline.

(II) Aniline $\longrightarrow$ acetanilide $\longrightarrow$ *p*-bromoacetanilide $\longrightarrow$ *p*-bromoaniline.

Quick Tip to Solve: For the first conversion remove the carboxyl carbon by Hofmann degradation; for the second protect, brominate, then hydrolyse.