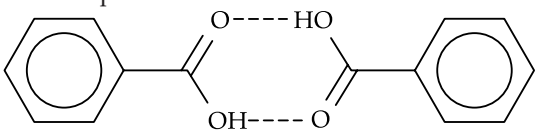
ANSWERS

SECTION – A

1. **Option (A) is correct.**

   ***Explanation*:** Association results in the formation of bigger molecules that are held together by intermolecular hydrogen bond and behave like a single particle. Consequently, the experimentally determined molar mass increases.

   For example: Benzoic acid exist a as a dimer:



2. **Option (B) is correct.**

   ***Explanation*:** The cell is represented as: $Cr/Cr^{3+}||Sn^{4+}/Sn^{2+}$

$$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$$
$$= 0.15 - (-0.74)$$
$$= +0.89\ V$$

3. **Option (B) is correct.**

   ***Explanation*:** Cr^{3+} = [Ar]$3d^3 4s^0$, it has 3 unpaired electrons.

$$\mu = \sqrt{n(n+2)} = \sqrt{3(3+2)}$$
$$= \sqrt{15} = 3.87\ BM$$

4. **Option (D) is correct.**

   ***Explanation*:** $5\,SO_3^{2-} + 2\,MnO_4^- + 6H^+ \longrightarrow 2Mn^{2+} + 3\,H_2O + 5\,SO_4^{2-}$

5. **Option (B) is correct.**

   ***Explanation*:** I.U.P.A.C. Name of ion will be:

   Diamminedichloridoplatinum(IV)

6. **Option (C) is correct.**

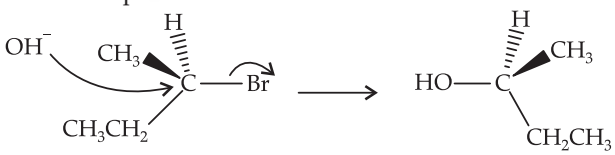
   ***Explanation*:** The boiling points of isomeric haloalkanes decrease with an increase in branching because the higher the branching in the haloalkanes, the smaller their surface area becomes. This, in turn, reduces the Van der Waals forced of attraction in the molecule.

   Order of boiling point:

   2-Bromo-2-methylpropane<1-Bromo-2-methyl propane<1-Bromobutane

7. **Option (C) is correct.**

   ***Explanation*:** Bimolecular mechanism in nucleophilic substitution is S_N2 which involves inversion of configuration, known as Walden inversion. Example:



(R) - 2 - Bromobutane (S) - 2 - Butanol

8. **Option (A) is correct.**

   ***Explanation*:** $C_6H_5OH > H_2O > ROH$

   The acidic nature depends on the stability of the conjugate base. Phenol forms a more stable phenoxide ion and is appreciably acidic.

   ROH is the least acidic, as its conjugate base RO^- is unstable than OH^- which is formed by H_2O, because of positive inductive effect of alkyl group.

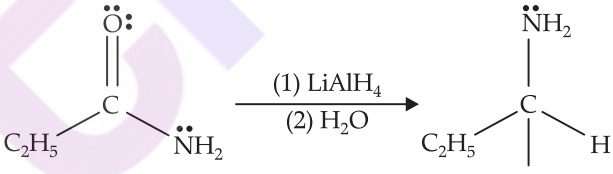
9. **Option (A) is correct.**

   ***Explanation*:** Butanoic acid is formed as per the reaction:

$$CH_3CH_2CH_2MgBr + CO_2 \longrightarrow CH_3—CH_2—CH_2—COOH^-\overset{+}{M}gBr \xrightarrow{H_2O/H^+} CH_3CH_2CH_2COOH + Mg(OH)Br$$

10. **Option (D) is correct.**

    ***Explanation*:** $LiAlH_4$ in ether acts as a good reducing agent and reduces amide to primary amines.



Propanamide Propanamine

11. **Option (D) is correct.**

    ***Explanation*:** It does not respond to Schiff's test, as glucose contains an aldehyde group in its open structure but forms a cyclic structure. This structure is quite stable and is not broken down by Schiff's reagent which is a weak base. Glucose exists primarily as pyranose structure but it also exists in furanose structure.

12. **Option (D) is correct.**

    ***Explanation*:** When a raw mango is placed in a concentrated salt solution, it loses water due to osmosis. It shrivels up and is used to make pickle. Water flows from a solution of lower concentration to higher concentration.

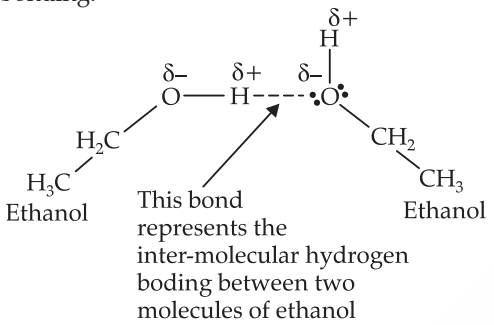
13. **Option (A) is correct.**

    ***Explanation*:** A homoleptic complex is one in which all the ligands (molecules or ions surrounding the central metal ion) are identical. Since, both of these complexes have only water molecules as ligands, they are indeed homoleptic complexes.

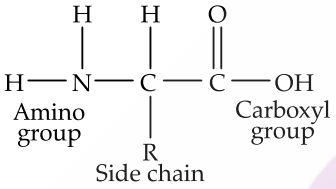
14. **Option (B) is correct.**

For the same alkyl group, the boiling point of haloalkanes decreases in the order:
RI>RBr>RCl>RF.
This is due to the increase in Van der Waals forces when the size and mass of the halogen atom increase.
The boiling point of alkyl halides are higher than hydrocarbon of comparable molecular mass because alkyl halides are polar while hydrocarbons are non polar in nature.

15. Option (C) is correct.
***Explanation*:** The boiling point of ethanol is higher than methoxymethane due to intermolecular hydrogen bonding and not intramolecular hydrogen bonding.



16. Option (B) is correct.
***Explanation*:** The optical activity is because of their asymmetric structure present in α alkyl substituted amino acids and not because of its *L* configuration.



SECTION – B

17. (A) (a) Pressure inside a pressure cooker is artificially increased. As the pressure inside the cooker rises, the boiling point of the liquid also increases. This higher temperature accelerates the cooking process significantly.

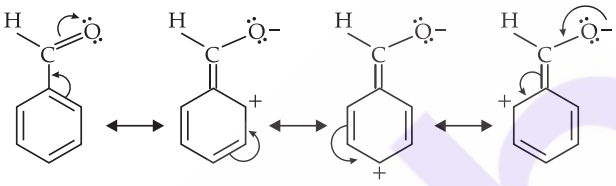
(b) On mixing *X* and *Y*, if the volume of the solution decreases, it means that the interaction between the *X*-*X* and *Y*-*Y* molecules reduces and the intermolecular interactions between *X* and *Y* increases. This leads to negative deviation of Raoult's law. Due to the decrease in vapour pressure, the boiling point of the solution increases. The temperature of the solution increases which means $\Delta H = -$ve.
So, it is an exothermic reaction.

OR

(B) Azeotropes: Azeotropes are binary mixture that have the same composition in the liquid and vapour phases and boil at constant temperatures. Azeotropes showing negative deviation from Raoult's law form maximum boiling azeotropes at a specific composition.
Example: Azeotrope formed from nitric acid and water.

18. (a) $2MnO_4^- + 10I^- + 16H^+ \longrightarrow 2Mn^{2+} + 8H_2O + 5I_2$
(b) $Cr_2O_7^{2-} + 14H^+ + 6Fe^{2+} \longrightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O$

19. Benzaldehyde is less reactive than propanal towards nucleophilic addition reactions.
In benzaldehyde, there is a resonance of carbonyl group which withdraw electron cloud towards itself, reducing the electrophilicity of the carbonyl carbon.

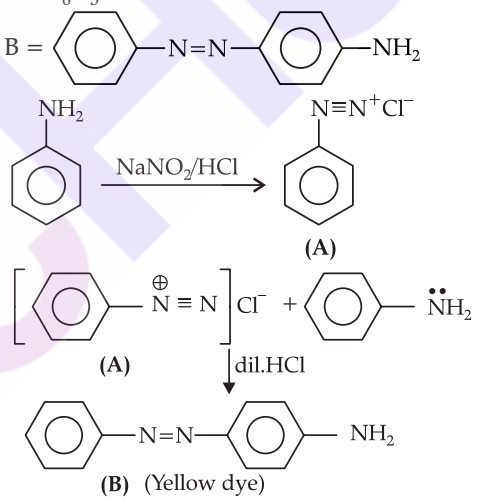


20. (a) $A = CH_3CH_2CN$
$B = CH_3CH_2CH_2NH_2$

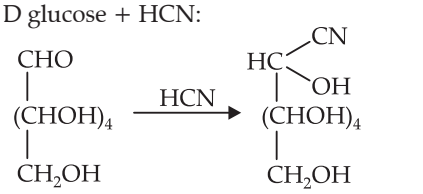
$$CH_3CH_2Cl + NaCN \rightarrow CH_3CH_2CN \xrightarrow{H_2/Ni} CH_3CH_2CH_2NH_2$$

Ethyl cyanide (A) — Propanamine (B)

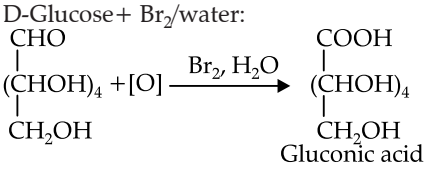
(b) $A = C_6H_5N^{2+}Cl^-$



21. (a) D glucose + HCN:



(b) D-Glucose + Br_2/water:



SECTION – C

22. T_b of glucose solution = 100.20°C,

$\Delta T_b = 100.20 - 100 = 0.20°C$
$\Delta T_b = K_b \times m$ (where, m = molality)
$m = 0.20/0.512$ $m = 0.390$ mol/kg
$\Delta T_f = K_f \times m = 1.86 \times 0.390$
$= 0.725$ °C

Freezing point of solution = 0 – 0.725 = –0.725 °C

23. (a) (i) Kohlrausch's law states that the molar conductivity of an electrolyte at infinite dilution is equal to the sum of the limiting molar conductivity of the anions and cations.

$\Lambda^\circ_m = \nu_+ \lambda^\circ_+ + \nu_- \lambda^\circ_-$

Here λ°_+ and λ°_- are limiting molar conductivities of cations and anions.

(ii) Faraday's First Law of Electrolysis: The mass of a substance deposited at any electrode is directly proportional to the amount of charge passed.

(b) As corrosion is a phenomenon involving the oxidation of iron, it is essential to consider the oxidation potentials of all elements. An element with a higher oxidation potential than Fe will oxidise faster than iron preventing corrosion in iron.

As per given data, oxidation potential of: $E^\circ_{Fe^{2+}/Fe} = -0.44$ V, $E^\circ_{X^{2+}/X} = -2.36$ V, $E^\circ_{Y^{2+}/Y} = -0.14$ V

As $E^\circ_{X^{2+}/X}$ has higher oxidation potential than iron, it can be used for coating the surface of iron.

24.
$$t_{1/2} = 0.693/k$$
$$k = 0.693/t_{1/2}$$
$$k_1 = 0.693/20 = 0.03465\ min^{-1}$$
$$k_2 = 0.693/5 = 0.1386\ min^{-1}$$
$$\log k_2/k_1 = \frac{E_a}{2.303R} \times \left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

substituting the values:

$\log 4 = E_a \times 50/2.303 \times 8.314 \times 300 \times 350$

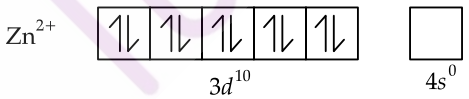
$0.602 = E_a \times 50/2.303 \times 8.314 \times 300 \times 350$

$E_a = 0.602 \times 2.303 \times 8.314 \times 2100 = 24205.8$ J/mol

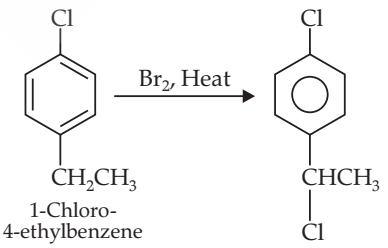
25. (a) The sum of enthalpy of atomization and ionisation enthalpy for copper is higher than hydration enthalpy due to this copper has positive value of $E^\circ_{Cu^{+2}/Cu}$.

(b) Cr, because Cr^{2+} which has $[Ar]3d^4 4s^0$ configuration, tends to lose one more electron forming Cr^{3+} to attain the more stable half-filled $t^3_{2g}(d^3)$ configuration. This is proved by its negative reduction potential value.

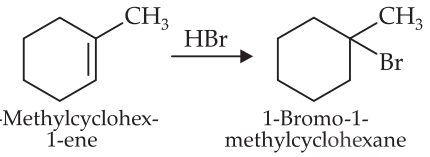
(c) Zn in its +2 state has the configuration $[Ar]3d^{10}4s^0$, indicating all electrons are paired in *d* orbitals. This does not allow *d–d* transition to occur and its salts are thus colourless.



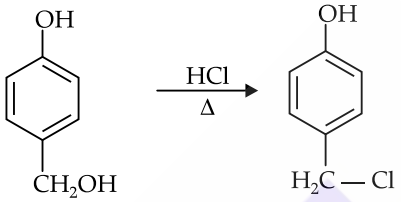
26. (A) (a)



(b)

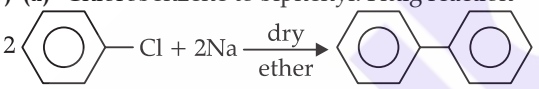


(c)



OR

(B) (a) Chlorobenzene to biphenyl: Fittig reaction



(b) Propene to 1-Iodopropane

$$CH_3CH = CH_2 + HBr \xrightarrow{H_2O_2} CH_3CH_2CH_2Br$$

$$CH_3CH_2CH_2Br + NaI \xrightarrow{\text{acetone}} CH_3CH_2CH_2I + NaBr$$

(c) 2 bromo butane to but-2-ene

$CH_3CH(Br)CH_2CH_3$ + alcKOH $\longrightarrow$ $CH_3CH = CHCH_3 + KBr + H_2O$

27. (a) Stronger intermolecular H-bonding results in associated molecules that have higher boiling points.

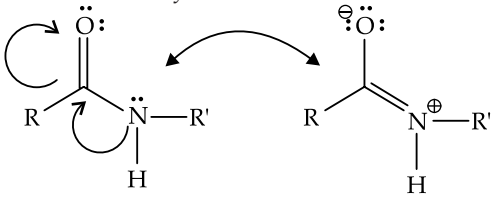
Alcohol > Amine, as O—H bond is more polar than N—H bond.

Thus, the increasing order of boiling point is:

$(CH_3)_2NH < CH_3CH_2NH_2 < CH_3CH_2OH$

(b) (i) Aromatic primary amines cannot be formed by this reaction as the aryl halides do not undergo nucleophilic substitution with potassium phthalimide which involves the cleavage of C—X bond. Aryl halides have double bond character in C—X bond.

(ii) In amides, the lone pair of nitrogen is involved in resonance with the carbonyl group and is not available for coordinate bond formation with a proton. But, in amine the lone pair of nitrogen available for protonation that's why amides are less basic than amines.



28. (a) Protein found in a biological system with unique three-dimensional structure and biological activity is called native protein.

When a protein in its native form is subjected to changes in temperature, etc, its structure is destroyed and it loses its biological activity. The protein thus formed is called denatured protein.

(b) Lactose

(c) Vitamin K

SECTION – D

29. (a) (i) The rate determining step is the slowest step of a chemical reaction that determines the speed at which the overall reaction proceeds.

(ii) When overall reaction does not occur in a single step, but occurs in multiple steps, such that order is not equal to the molecularity of the reaction. The mechanism of a complex reaction consists of more than one elementary step, and it may involve the formation of complex compounds or intermediates.

(b) With increase in temperature, the rate of the reaction and the rate constant increases.

OR

(b) A complex reaction proceeds through several elementary reactions. The number of molecules involved in each elementary reaction may be different, i.e., the molecularity of each step may be different. Therefore, it is impossible to determine the molecularity of overall complex reaction. Order of a complex reaction is determined by the slowest step in its mechanism and is not dependent on the number of steps involved in a reaction.

(c) For the reaction, $X \rightarrow Y$

For second order,

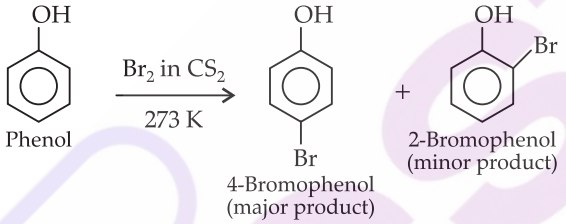
Rate = $k[X]^2$, X = a mol/litre

When the concentration of X is increased three times, then $[X] = 3a$ mol/L

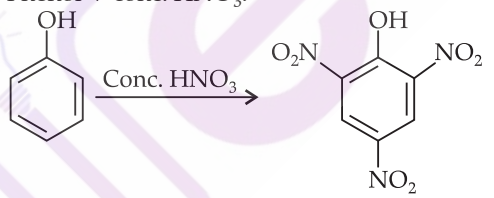
Rate = $k\,(3a)^2 = 9\,ka^2$

Thus, the rate of formation of Y will become 9 times.

30. (a) (i) Phenol + Br_2/CS_2:

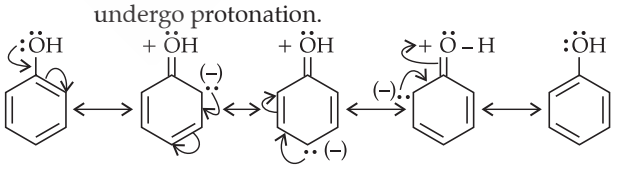


(ii) Phenol + conc. HNO_3:



2, 4,6-Trinitrophenol
(Picric acid)

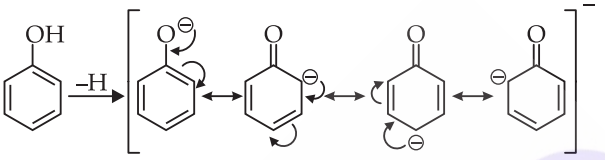
(b) One lone pair of oxygen in phenol is involved in resonance with benzene ring, thus generating a positive charge on oxygen. It will not easily undergo protonation.



I II III IV V

(c) Phenol is a stronger acid. In cresol, due to +I effect and hyper conjugation effect of methyl group, the density of electron towards oxygen atom increases, destabilising the conjugate base.

While in phenol, the phenoxide ion is resonance stabilised and that makes it a stronger acid than cresol.



OR

(c) The product is salicylaldehyde: IUPAC : 2-Hydroxybenzaldehyde

SECTION – E

31. (A) (a) At anode: $Sn \rightarrow Sn^{2+} + 2e^-$

At cathode: $2H^+ + 2e^- \rightarrow H_2$

$E°cell = E°_{SHE} - E°_{Sn^{2+}/Sn}$

$= 0 - (-0.14)$

$= +0.14$ V

$E_{cell} = E°_{cell} - 0.0591/2 \log [Sn^{2+}] \times P_{H_2}/[H^+]^2$

$= 0.14 - 0.0591/2 \log 0.004 \times 0.987/[0.020]^2$

$= 0.111$V

(b) (i) On the basis of $E°$ values, O_2 gas should be liberated at anode but it is Cl_2 gas which is liberated in the electrolysis of aqueous NaCl. It is due to the phenomenon of over-voltage. Experimentally, it is observed that the actual voltage required for electrolysis is greater than that calculated from standard potentials. This addition voltage required is called over-voltage. It is required because the rate of transfer of electrons at the interface of electrode and solutions for both half reactions is slow. The over-voltage required for formation of oxygen is much larger than that required for the formation of chlorine.

(ii) Acetic acid (CH_3COOH) is known as a weak electrolyte because it ionizes only partially when dissolved in water. During dilution, the number of ions per unit volume decreases, despite an increase in the degree of ionization. Since the number of free ions in the solution affects conductivity, dilution leads to a decrease in overall conductivity even though ionization increases.

(B) (a) Anode: $Pb + SO_4^{2-} \rightarrow PbSO_4 + 2e^-$

Cathode: $PbO_2 + SO_4^{2-} + 4H^+ + 2e^- \rightarrow PbSO_4 + 2H_2O$

Overall cell reaction:

$Pb + PbO_2 + 4H^+ + 2SO_4^{2-} \rightarrow 2PbSO_4 + 2H_2O$

(b) $E_{cell} = E°_{cell} - 0.0592/n \log \dfrac{[Cr^{+3}]^2}{[Cr_2O_7^{-2}][H^+]^{14}}$

Substituting,

$= 1.33 - 0.0591/6 \log [0.01]^2/[0.01][10^{-4}]^{14}$

$= 1.33 - 0.0591/6\,[54 \log 10]$

$= 1.33 - 0.0591/6\,[54 \times 1]$

$= 0.7981$ V

32. (A) (a) A tetrahedral compound has sp^3 hybridisation, where four ligands form a tetrahedron structure around the metal ion. During crystal field splitting, the *d*-orbitals split into two groups – one with a higher energy and the other with a lower energy.

Since, the ligands in a tetrahedral complex do not approach the *d*-orbitals directly, instead they approach between the axis, the splitting energy of *d* orbitals is much lower than that of the pairing energy, and thus the electrons jump to the higher energy level *d*-orbitals rather than pairing, resulting in high-spin complexes being formed.

(b) Co^{3+} can be oxidised to Co^{3+} in the presence of strong field ligands. Strong field ligands, such as CN^- (cyanide) or CO, create a strong ligand field that stabilizes the higher oxidation state of the metal ion. This stabilisation occurs because strong field ligands cause a significant splitting of the *d*-orbitals, making the +3 oxidation state more favourable.

(c) Coordination isomerism

In coordination isomerism, both positive and negative ions of a salt are complex ions and the two isomers differ in the distribution of ligands between the cation and the anion.

(d) In both complexes, Ni is in +2 oxidation state with a valence shell electronic configuration of $3d^8$. In the presence of weak field water ligands, two unpaired electrons do not pair up. The $[Ni(H_2O)_6]^{2+}$ has two unpaired electrons which result in green colour, due to *d*–*d* transition.

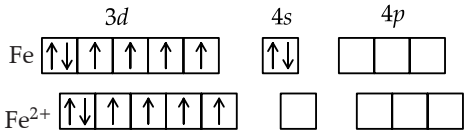
In presence of strong field cyanide ligand, the unpaired electrons in 3*d* orbital pair up. Due to an absence of unpaired electrons, no *d*–*d* transitions are possible and the $[Ni(CN)_4]^{2-}$ is colourless.

(e) Pentaamminecarbonatocobalt(III)chloride

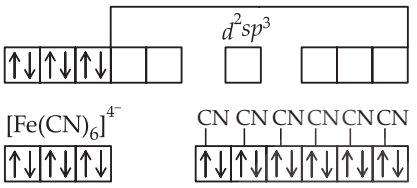
OR

(B) (a) When a ligand uses its two or more donor atoms, simultaneously a ring-like structure is formed. The formation of such ring-like structures is called a chelate effect. Compounds having chelate rings are more stable as compared to other compounds.

(b) The hybridisation is d^2sp^3 and it forms an inner orbital complex. Since, there are no unpaired electrons, the complex is diamagnetic and there is no resultant magnetic moment.



Hybridisation



(c) $[Pt(NH_3)_2Cl_2]$

33. (A) (a) (i) Ethanal to But-2-enal by aldol condensation:

$$2CH_3\text{–}CHO \xrightarrow{\text{dil.NaOH}} \underset{\text{3-Hydroxybutanal}}{CH_3\text{–}CHOH\text{–}CH_2\text{–}CHO}$$

Ethanal

$$CH_3\text{–}CHOH\text{–}CH_2\text{–}CHO \xrightarrow{H^+} \underset{\text{But-2-enal}}{CH_3\text{–}CH{=}CH\text{–}CHO} + H_2O$$

3-Hydroxybutanal

(ii) Propanoic acid to ethane

$$CH_3CH_2COOH \xrightarrow{NH_3/\text{Heat}} CH_3CH_2CONH_2 \xrightarrow{Br_2/KOH} CH_3CH_2NH_2 \xrightarrow{HNO_2} CH_3CH_2OH$$

$$\xrightarrow{\text{conc. } H_2SO_4/170^\circ C} CH_2{=}CH_2 \xrightarrow{H_2/Ni} H_3C\text{—}CH_3$$

(b) A = $CH_3CH = C(CH_3)_2$,
B = CH_3CHO,
C = CH_3COCH_3

$$\underset{\text{(A)}}{CH_3CH{=}\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{C}}}\text{–}CH_3} \xrightarrow[\text{(ii) } Zn/H_2O]{\text{(i) } O_3} \underset{\text{(B)}}{CH_3CHO} + \underset{\text{(C)}}{CH_3\text{–}\overset{\displaystyle O}{\overset{\|}{C}}\text{–}CH_3}$$

$$CH_3CHO + 3I_2 + 4NaOH \rightarrow \underset{\text{(B)}}{HCOONa} + CHI_3 + 3NaI + 3H_2O$$

$$CH_3COCH_3 + 4NaOH + 3I_2 \rightarrow \underset{\text{(C)}}{CHI_3} + 3NaI + 3H_2O + CH_3COONa$$

OR

(B) $\underset{(C_8H_{16}O_2)}{A} \xrightarrow[\text{dil. } H_2SO_4]{\text{hydrolysed}} \underset{\text{(B)}}{\text{carboxylic acid}} + \underset{\text{(C)}}{\text{alcohol}}$

A ⟶ ester (butyl butanoate)

$$\underset{\text{(A)}}{CH_3CH_2CH_2COOCH_2CH_2CH_2CH_3} + H_3O^+ \longrightarrow \underset{\text{(B)}}{CH_3CH_2CH_2COOH} + \underset{\text{(C)}}{CH_3CH_2CH_2CH_2OH}$$

B ⟶ Butanoic acid
C ⟶ Butan-1-ol

$CH_3CH_2CH_2CH_2OH$ (C)

Dehydration ($-H_2O$)	Oxidation H_2CrO_4
$CH_3CH_2CH = CH_2$	$CH_3CH_2CH_2COOH$
But-1-ene	Butanoic acid (B)