Answers to 2023 JC2 Preliminary Examination H2 Chemistry (9729) Paper 3

1 **(a)** $2CO + 2NO \rightarrow 2CO_2 + N_2$ **[1m]**

(b) The permanent dipole-permanent dipole attractions between CO molecules are stronger than the instantaneous dipole-induced dipole attractions between N_2 molecules and hence, more significant / is not negligible. **[2m]**

(c) **(i)**

$$\text{Amount of CO gas} = \frac{364}{(12.0+16.0)} = 13.0 \text{ mol}$$

$$\text{Amount of } H_2 \text{ gas} = \frac{5}{2(1.0)} = 2.50 \text{ mol}$$

$$\text{Amount of } CH_3OH \text{ gas} = \frac{171}{(12.0+4.0+16.0)} = 5.34 \text{ mol}$$

Total amount of gas = 13.0 + 2.50 + 5.34 = 20.84 mol

$$\text{Mole fraction of CO} = \frac{13.0}{20.84} = 0.624$$

$$\text{Mole fraction of } H_2 = \frac{2.50}{20.84} = 0.120$$

$$\text{Mole fraction of } CH_3OH = \frac{5.34}{20.84} = 0.256$$

[1m] for all three mole fractions

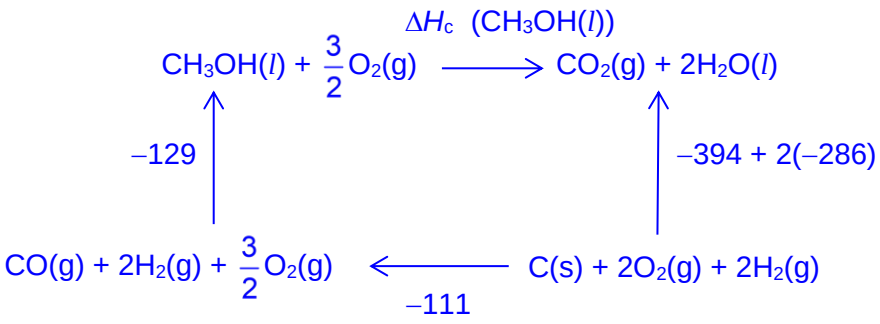
$$K_p = \frac{P_{CH_3OH}}{P_{CO}.(P_{H_2})^2} = \frac{0.256\times 60}{(0.624\times 60).(0.120\times 60)^2} = 7.91 \times 10^{-3} \text{ atm}^{-2}$$

[1m] Partial pressure of all three gases calculated

[1m] value of K_p

(ii) Increasing the temperature shifts the position of equilibrium to the left to favour the backward endothermic reaction so as to absorb some heat. The equilibrium yield of methanol decreases. **[1m]**

(d) **(i)**



[2m] cycle

ΔH_c $(CH_3OH(l))$

= -(-129) – (-111) + (-394) + 2(-286) = –726 kJ mol^{-1} **[1m]**

(d) **(ii)** Methanol is a liquid and is easier to transport / Synthesis gas is gaseous state, need to be stored under pressure. **[1m]**

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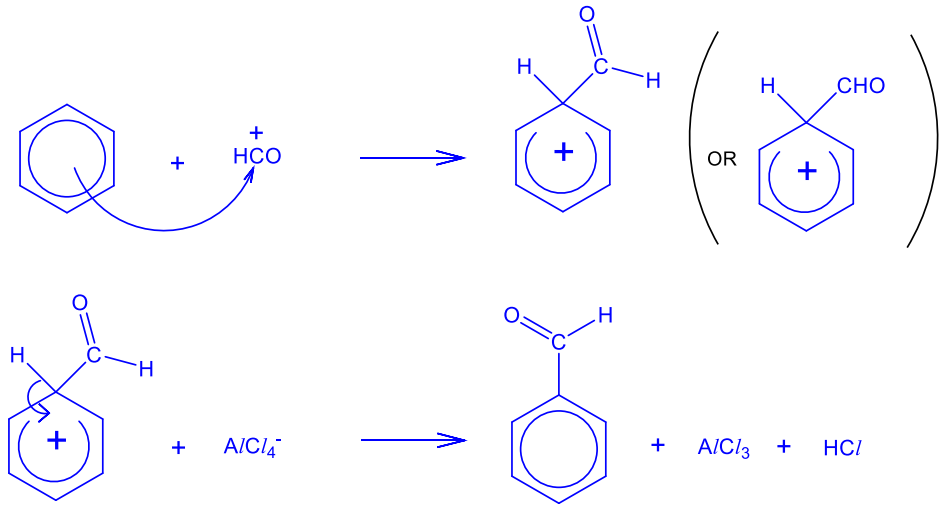
1 **(e)** **(i)** $HCOCl + AlCl_3 \rightarrow HCO^+ + AlCl_4^-$ **[1m]**

(ii)

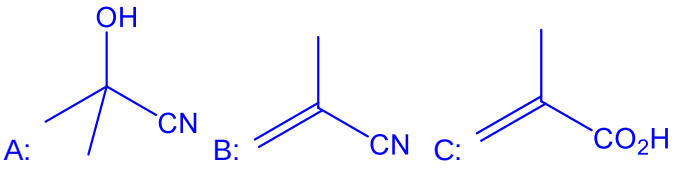


[2m] mechanism

- **full arrow from π–electrons of benzene ring to C of HCO^+ electrophile**
- **correct arenium ion + delocalisation of +ve charge over the 5 sp^2 C**
- **full arrow from the σ–bond of C–H bond to the +ve charge of arenium ion.**
- **correct product formed + balanced eqn with the regeneration of $AlCl_3$ catalyst.**

(iii) To retain the extra stability due to the delocalised π electron cloud of benzene ring, benzene favours substitution reaction over addition reaction which would otherwise, destroy the delocalised 6π electron cloud and its associated stability. **[1m]**

(i)



[1m] for each structure

(ii) Step 1: HCN, trace amount of NaCN / KCN / NaOH / KOH

Step 3: HCl(aq) / H_2SO_4(aq), heat

[1m] each

2 **(a)** They have giant covalent structure.

Decreasing amount of energy is required to overcome the decreasing strength of covalent bonds between the respective atoms due to increase in radius from C to Ge, resulting in an increase in bond length between their respective atoms.

Hence, the melting points decreases from carbon to germanium. **[2m]**

(b) $SiCl_4$ hydrolyses completely in water to give an acidic solution of pH 1. A solid forms.

Hydrolysis: $SiCl_4(l) + 2H_2O(l) \rightarrow SiO_2(s) + 4HCl$ (aq)

$AlCl_3$, dissolves to give $[Al(H_2O)_6]^{3+}$ which hydrolyses partially in water to give an acidic solution of pH 3.

Hydration : $AlCl_3(s) + 6H_2O(l) \rightarrow [Al(H_2O)_6]^{3+}(aq) + 3Cl^-(aq)$

Hydrolysis : $[Al(H_2O)_6]^{3+}(aq) \ll [Al(H_2O)_5OH]^{2+}(aq) + H^+(aq)$

[3m]

2 **(c)** The larger the K_a value, the stronger the acid.

HCO_2H is a stronger acid than CH_3CO_2H as the electron-donating -CH_3 group intensifies the negative charge on CH_3COO^-, making it less stable than $HCOO^-$.

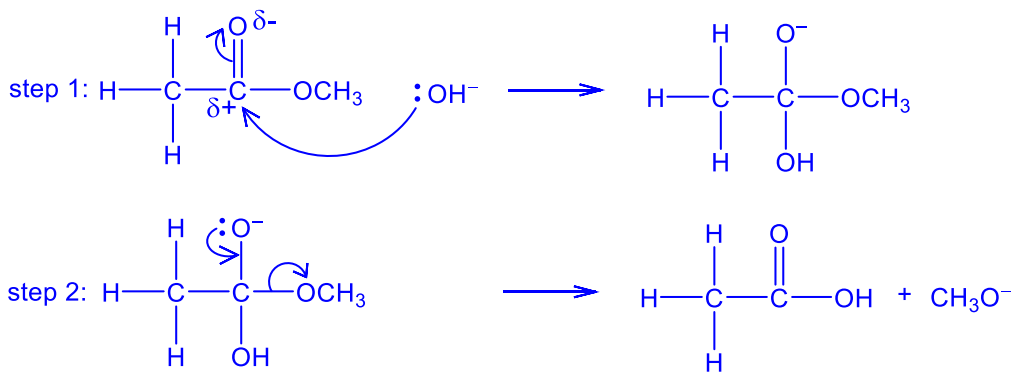
Methanesulfonic acid is a stronger acid than ethanoic acid as the negative charge of $CH_3SO_2O^-$ can be delocalised over more oxygen atoms, dispersing the negative charge and making $CH_3SO_2O^-$ more stable.

OR

Methanesulfonic acid is a stronger acid than ethanoic acid as it has an additional electron-withdrawing oxygen atom attached to S, which helps to disperse the negative charge and making $CH_3SO_2O^-$ more stable.

[2m]

(d) **(i)**



[3m] mechanism

- **δ+ on C and δ– on O of C=O bond**
- **full arrow from lone pair from O of OH^- to the $^{\delta+}$C of C=O group**
- **full arrow from π–bond of C=O to the $^{\delta-}$O of C=O group**
- **correct negatively charged intermediate**
- **full arrow from lone pair on O^- of intermediate to form C=O bond**
- **full arrow from C–O bond to O of –OCH_3 group**
- **correct carboxylic acid and alkoxide products formed**

(ii) The three methyl groups bonded to the carbon adjacent to the ester group results in steric hindrance, which makes it more difficult for the OH^- nucleophile to approach the C=O of the ester group.

OR

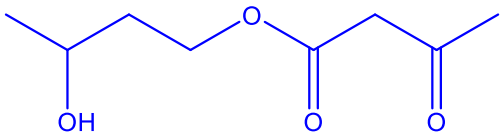
The $(CH_3)_3C$- group is more electron-donating than -CH_3, making the carbon of C=O of the ester group less electron-deficient and less easily attacked by the OH^- nucleophile.

[1m]

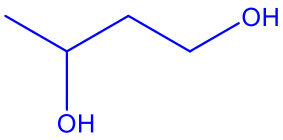
2 (e)

Information	Type of reaction	Deduction
Ester D is hydrolysed by aqueous alkali, followed by acidification to give E and F.	alkaline hydrolysis	The organic products are alcohol and carboxylic acid.
F reacts with Na_2CO_3(aq) but E does not.	acid-carbonate / acid-base reaction	F has carboxylic acid / -COOH group. E has alcohol group.
F gives orange ppt with 2,4-DNPH but E does not.	condensation	F contains ketone or aldehyde group but not E
F does not react with Fehling's solution.	-	F is not an aliphatic aldehyde. F contains ketone group.
E reacts with acidified $K_2Cr_2O_7$ on prolonged heating to give F.	oxidation	E has a secondary alcohol group and a primary alcohol group. Both E and F have four carbon atoms each.
D, E and F reacts with alkaline I_2(aq) to give yellow ppt.	oxidation with alkaline I_2(aq) / positive iodoform test	F is a ketone with -$COCH_3$ group E has -$CH(OH)CH_3$ group D also have the above groups.

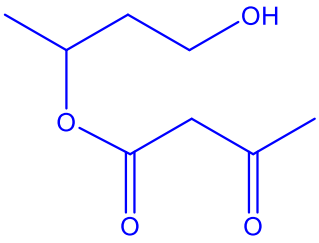
Reasoning [4m]



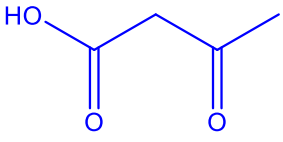
OR



compound **E**



compound **D**



compound **F**

[1m] for each correct structure

2 (f) (i) Amount of Sn^{2+} in 25.0 cm^3 of H

$= \frac{5}{2} \times \frac{18.50}{1000} \times 0.020 = 9.25 \times 10^{-4}$ mol **[1m]**

Amount of Sn^{2+} in 25.0 cm^3 of the solution treated with H_2

$= \frac{5}{2} \times \frac{27.70}{1000} \times 0.020 = 1.39 \times 10^{-3}$ mol **[1m]**

(ii) Amount of Sn^{4+} originally present in H

$= 1.385 \times 10^{-3} - 9.25 \times 10^{-4} = 4.60 \times 10^{-4}$ mol

Ratio of Sn^{4+} : Sn^{2+}

$= 4.60 \times 10^{-4} : 9.25 \times 10^{-4} = 0.50$ **[1m]**

Average oxidation number of Sn in the oxide = $\frac{1}{3}\{1(+4) + 2(+2)\} = +\frac{8}{3}$

Sn : O ratio = 8/3 : 2 = ¾ : 1 = 3: 4

Alternatively, 1 Sn^{4+}: 2 O^{2-} and 2 Sn^{2+} : 2 O^{2-} $\Rightarrow$ 3 Sn : 4 O

The formula of oxide C is Sn_3O_4. **[1m]**

3 (a) (i) $10NaN_3 + 2KNO_3 \rightarrow 16N_2 + 5Na_2O + K_2O$

Amount of NaN_3 : amount of N_2 = 1 : 1.6

Using idea gas equation, amount of N_2 gas to give the pressure required is n.

PV = nRT

$n = \frac{1.50 \times 10^5 \times 75.0 \times 10^{-3}}{8.31 \times (35.0 + 273)} =$ 4.40 mol **[1m]**

Amount of NaN_3 required = $4.40 \times \frac{1}{1.6} \times (23.0 + 42) = 179$ g **[2m]**

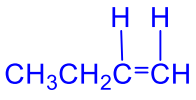
(ii) $SiO_2 + K_2O \rightarrow K_2SiO_3$

OR $SiO_2 + Na_2O \rightarrow Na_2SiO_3$ **[1m]**

(iii)

[1m]

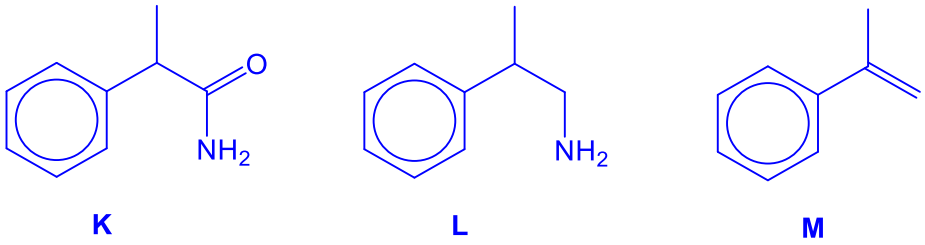
(b) (i)



[1m]

3 **(b)** **(ii)** Step 1: LiAlH$_4$, dry ether **[1m]**

Step 3: cold, alkaline KMnO$_4$ **[1m]**



K **L** **M**

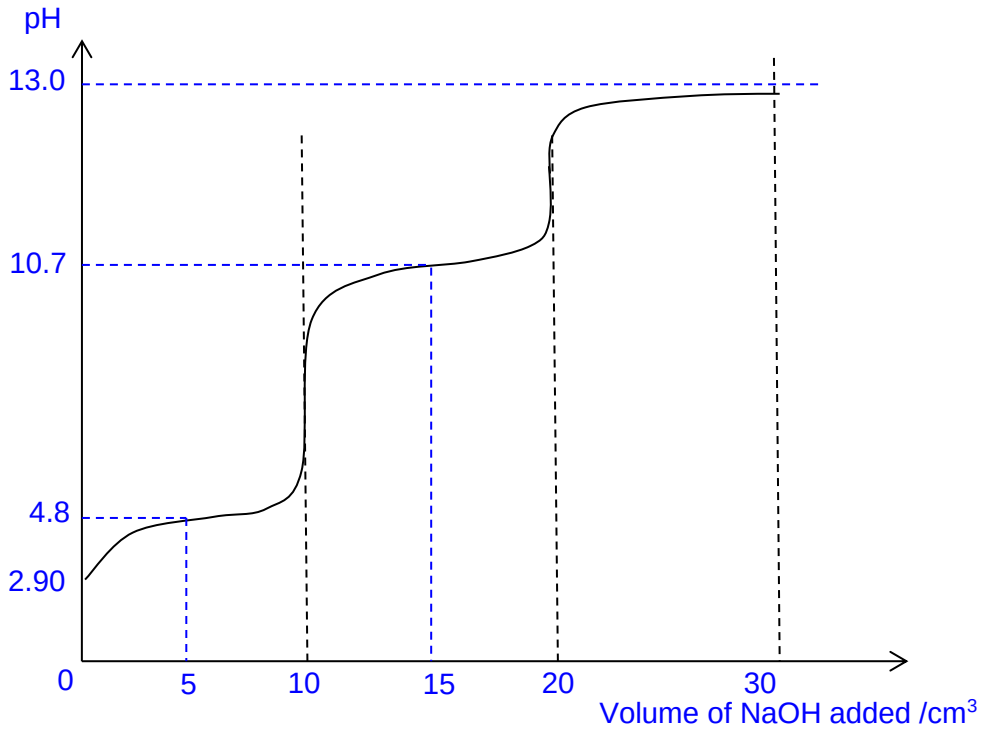
[1m] for each correct structure

(c) **(i)** $K_{a1} = 10^{-pKa1} = 10^{-4.8} = 1.58 \times 10^{-5}$ mol dm^{-3}

$[H^+] = \sqrt{1.58\times10^{-5}\times0.10} = 1.26 \times 10^{-3}$ mol dm^{-3}

pH = -lg(1.25 $\times$ 10^{-3}) = 2.9 or 2.90 **[1m]**

(ii)



[3m]

(d) **(i)** 3Ba(NH$_2$)$_2$ $\rightarrow$ Ba$_3$N$_2$ + 4NH$_3$ **[1m]**

(ii) Ca^{2+} has a smaller radius and hence, a higher charge density than Ba^{2+}.

The ability of Ca^{2+} to polarise the electron cloud of the large NH_2^- anion and weaken the N-H bonds in NH_2^- is greater than that of Ba^{2+}.

Hence, Ca(NH$_2$)$_2$ will decompose more readily. **[2m]**

4 **(a)** **(i)** The energy required / enthalpy change that occurs when 1 mole of electrons is removed from a mole of gaseous atoms to form a mole of singly charged gaseous ions. **[1m]**

(ii) From Sc to Cu, nuclear charge increases.

However, there is addition of electrons to an inner 3d subshell, which results in an increase in shielding effect by inner shell electrons.

Hence the nuclear attraction for the valence electrons remains approximately constant. **[1m]**

(iii) Cu: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^1$ Cu^+: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}$

Cr: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5\ 4s^1$ Cr^+: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5$

Both Cu and Cr have only one 4s electron while the rest of the transition elements have two 4s electrons. **[1m]**

The removal of the second electron for Cu and Cr comes from an inner principal quantum shell, which is closer and more strongly attracted to the nucleus compared to the 4s electron. **[1m]**

(b) **(i)**

	Co	N	H	Cl
% by mass	25.2	24.1	5.1	45.6
Amount / mol	$\frac{25.2}{58.9} = 0.428$	$\frac{24.1}{14.0} = 1.72$	$\frac{5.1}{1.0} = 5.10$	$\frac{45.6}{35.5} = 1.28$
Lowest ratio	1	4	12	3

Empirical formula of X is $CoN_4H_{12}Cl_3$ **[1m]**

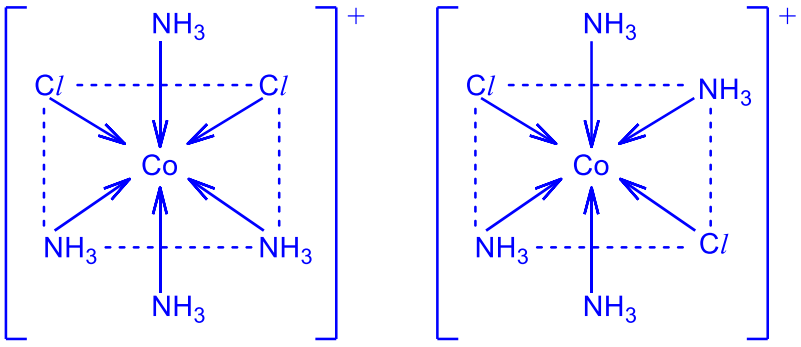
Since mol ratio of X : Cl = 1:1, one of the Cl in the empirical formula is a free chloride ion.

Ligands around cobalt atom in X are 4 NH_3 and 2 Cl^-

Complex ion in X is $Co(NH_3)_4Cl_2^+$ **[1m]**

Oxidation state of cobalt in X = +3 **[1m]**

(ii) Cis-trans isomerism **[1m]**

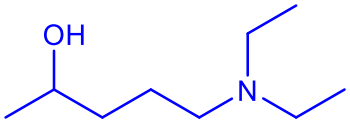


[1m] for both diagrams; ignore missing lone pairs on ligands

4 (c) (i) $(CH_3CH_2)_2NH$ **[1m]**

(ii) nucleophilic substitution **[1m]**

(iii)



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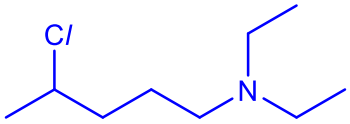


S

[1m] for each compound

Step 2: H_2, Ni catalyst, heat / $LiAlH_4$, dry ether / $NaBH_4$, methanol **[1m]**

Step 3: PCl_5, room temperature / PCl_3 / PBr_3 / $SOCl_2$, heat **[1m]**

Step 4: excess NH_3, ethanol, heat in sealed tube **[1m]**

(d) (i) N_y is more basic than N_x.

The lone pair of electrons on N_x is delocalised into the π electron system of the aromatic ring, making it less available for protonation.

There are more electron-donating alkyl groups on N_y, making the lone pair on N_y more available for protonation.

[2m]

(ii) Test: Add $K_2Cr_2O_7$(aq), H_2SO_4(aq) and heat. **[1m]**

Obs: Orange $K_2Cr_2O_7$ turns green for hydroxychloroquine but not for chloroquine **[1m]**

OR

Test: Add $KMnO_4$(aq), H_2SO_4(aq) and heat. **[1m]**

Obs: Purple $KMnO_4$ decolourises for hydroxychloroquine but not for chloroquine **[1m]**

OR

Test: Add PCl_5 **[1m]** – reject "heat"

Obs: White fumes of HCl for hydroxychloroquine but not for chloroquine **[1m]**

OR

Test: Add Na(s). **[1m]**

Obs: Effervescence of colourless odourless H_2 gas that gives pop sound with burning splint for hydroxychloroquine but not for chloroquine **[1m]**

5 **(a)** **(i)** $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^1$ **[1m]**

(ii) Since Cu^+ has more electrons, hence there is more interelectronic repulsion, thus Cu^+ has a larger ionic radius. **[1m]**

(iii) Presence of ligands cause the degenerate 3d orbitals to split into two different energy levels with relatively small energy difference. Radiation from the visible light region is absorbed when an electron transits from a d-orbital of lower energy to another partially filled d-orbital of higher energy. The colour observed is the complement of the colour absorbed. **[2m]**

Complexes of Cu(I) are colourless as they do not have partially-filled/unfilled d orbitals / have fully-filled 3d orbitals for the electrons to transit. **[1m]**

(b) **(i)** From *Data Booklet*:

$I_2 + 2e \ll 2I^-$ +0.54 V

$Cu^{2+} + e \ll Cu^+$ +0.15 V

$E^{\ominus}_{cell} = (+0.15) - (+0.54) =$ -0.39 V < 0 (not energetically feasible) **[1m]**

The white CuI precipitate formed decreases the concentration of Cu^+, causing position of equilibrium of $Cu^{2+} + e \ll Cu^+$ to shift right, making $E(Cu^{2+}/Cu^+)$ more positive. E_{cell} becomes more positive, thus reaction becomes feasible. **[1m]**

(ii) $CuI(s) \ll Cu^+(aq) + I^-(aq)$

Thiosulfate forms a stable complex/reacts with $Cu^+(aq)$, which causes $[Cu^+]$ to decrease and position of equilibrium of $CuI(s) \ll Cu^+(aq) + I^-(aq)$ to shift right, increasing the solubility of CuI. Thus precipitate dissolves. **[1m]**

(c) **(i)** Since value of K_{stab} is greater than 1, position of equilibrium lies to the right. **[1m]**

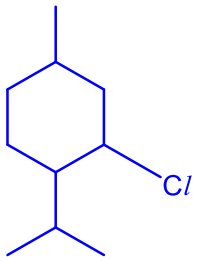
The stronger NH_3 ligand replaces the weaker H_2O ligand by forming a stronger dative bond and form a more stable $[Cu(NH_3)_4(H_2O)_2]^{2+}$complex ion. **[1m]**

(ii) When en is added, solution colour changes from dark blue to purple. **[1m]**

Since K_{stab} of $[Cu(en)(H_2O)_4]^{2+}$ is larger than that of $[Cu(NH_3)_4(H_2O)_2]^{2+}$, upon addition of ethane-1,2-diamine, the more stable $[Cu(en)(H_2O)_4]^{2+}$ is formed. **[1m]**

(d) **(i)** Step 1: PCl_5, room temperature / PCl_3 / PBr_3 / $SOCl_2$, heat **[1m]**

Step 2: NaCN, ethanol, heat **[1m]**



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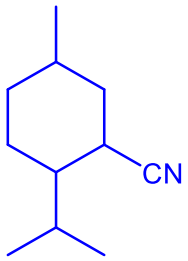


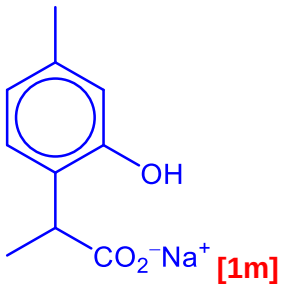
V

[1m] for each compound

(ii) Test: Add 2,4–DNPH. **[1m]**

Obs: Orange ppt formed for menthone but not menthol **[1m]**

5 (e) (i)



[1m]

(ii) Phenol is a weaker acid than H_2CO_3, hence acid-base reaction with HCO_3^- does not occur. **[1m]**

OR

Carboxylic acid is a stronger acid than H_2CO_3, hence, acid-base reaction with HCO_3^- occurs. **[1m]**