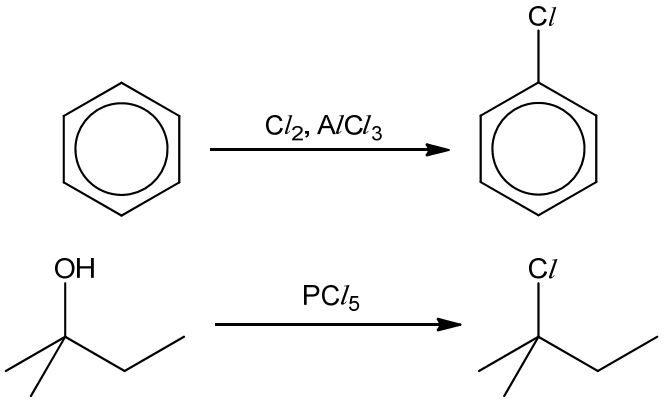
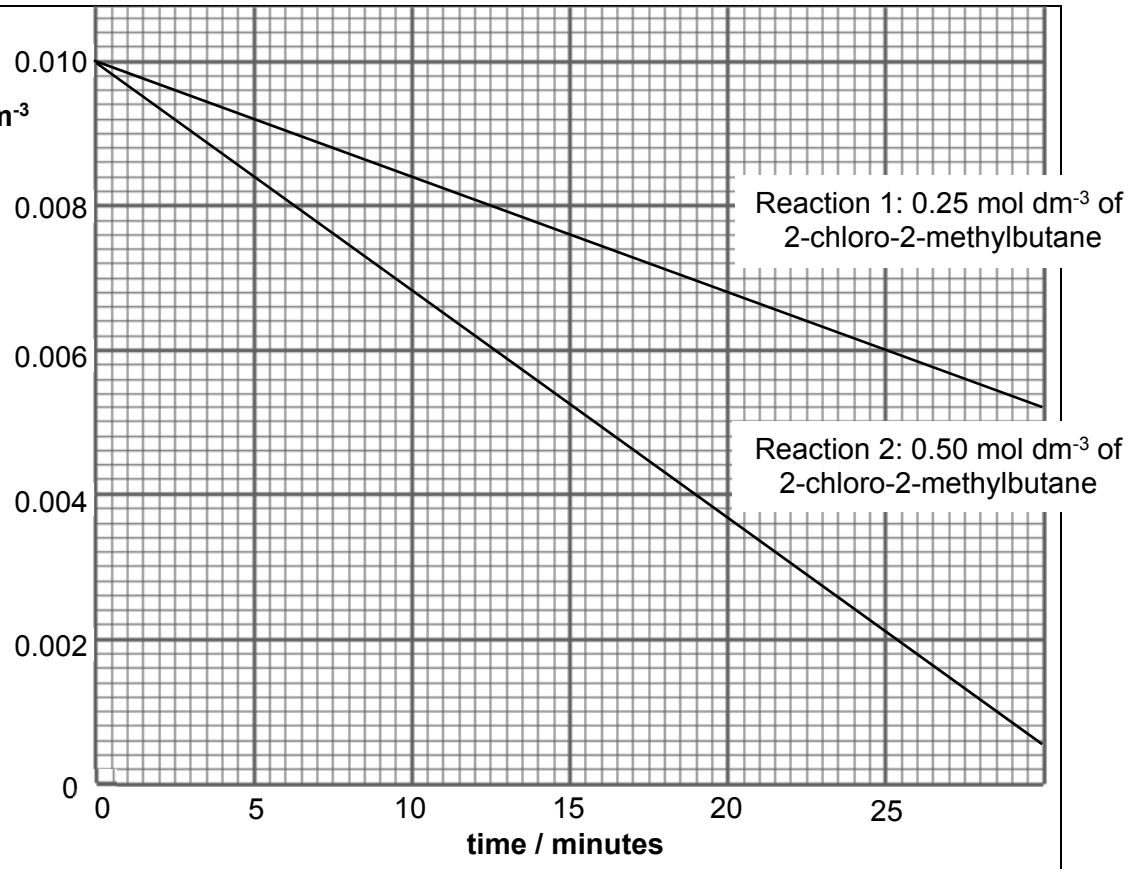
Section A
Answer **all** questions in this section.

1	**(a)**	**(i)**	Due to reactivity of A*l*C*l*$_3$ and PC*l*$_5$ in water, the following reactions are carried out under anhydrous conditions.  Write equations showing the reactions of aluminium chloride and phosphorus pentachloride in water. State the pH of resulting solutions. [3]
			A*l*C*l*$_3$ + 6H$_2$O ⟶ [A*l*(H$_2$O)$_6$]$^{3+}$ + 3C*l*$^-$ **[A*l*(H$_2$O)$_6$]$^{3+}$ ⇌ [A*l*(H$_2$O)$_5$(OH)]$^{2+}$ + H$^+$** **pH 3** **PC*l*$_5$ + H$_2$O ⟶ POC*l*$_3$ + 2HC*l*** **POC*l*$_3$ + 3H$_2$O ⟶ H$_3$PO$_4$ + 3HC*l*** **OR PC*l*$_5$ + 4H$_2$O ⟶ H$_3$PO$_4$ + 5HC*l*** **pH 2**
		(ii)	Chlorobenzene and 2-chloro-2-methylbutane are separately boiled with aqueous sodium hydroxide and acidified with nitric acid before aqueous silver nitrate is added. State and explain the difference in observations. Write equations for the reactions that occur. [3]
			2-chloro-2-methylbutane forms a white ppt while chlorobenzene does not. **The C–C*l* bond in chlorobenzene is strengthened by partial double bond character due to the overlap of p-orbital on C*l* atom and π-orbital of benzene. Hence chlorobenzene is resistant to hydrolysis.** **CH$_3$C(CH$_3$)C*l*CH$_2$CH$_3$ + OH$^-$ ⟶ CH$_3$C(CH$_3$)OHCH$_2$CH$_3$ + C*l*$^-$** **Ag$^+$ + C*l*$^-$ ⟶ AgC*l***
	(b)	**(i)**	To study the kinetics of the reaction between 2-chloro-2-methylbutane and sodium hydroxide in alcoholic medium, two experiments with different initial concentrations of 2-chloro-2-methylbutane were carried out at constant temperature. A [NaOH]–time graph was plotted using the results obtained from the experiments.



(i) Deduce the order of reaction with respect to 2-chloro-2-methylbutane and NaOH. [2]

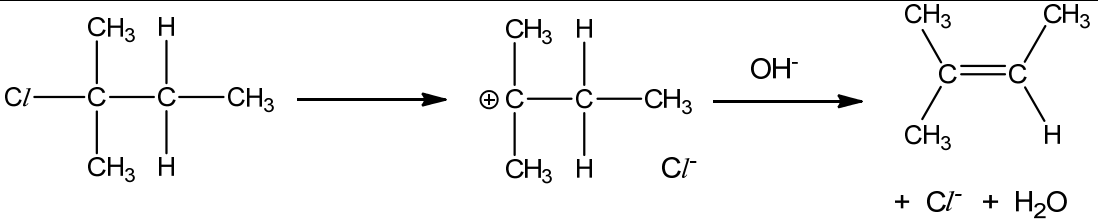
Using Reaction 1 (or 2), when [NaOH] decreases, gradient remains constant, hence rate of reaction is constant. Rate of reaction is independent of [NaOH], hence the reaction is zero order wrt [NaOH].

Comparing reactions 1 and 2, when [2-chloro-2-methylbutane] doubles from 0.25 to 0.50 mol dm^{-3}, the gradient doubles, showing that the rate of reaction doubles from 1.60×10^{-4} to 3.15×10^{-4} mol dm^{-3} min^{-1}. Rate of reaction $\propto$ [2-chloro-2-methylbutane], hence the reaction is first order wrt [2-chloro-2-methylbutane].

(ii) Hence, state the rate equation of this reaction. [1]

Rate = k[2-chloro-2-methylbutane]

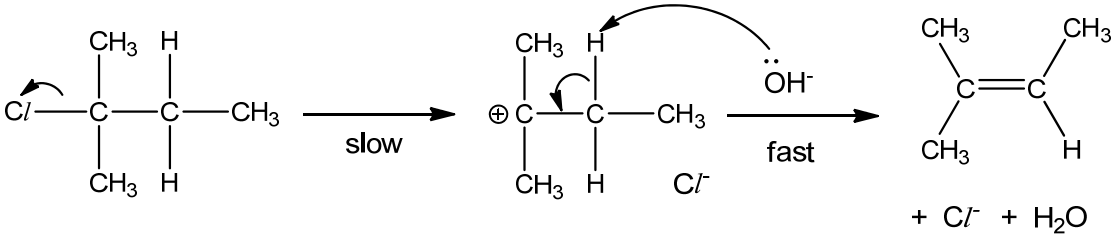
(iii) The proposed mechanism of 2-chloro-2-methylbutane with alcoholic sodium hydroxide is given below.



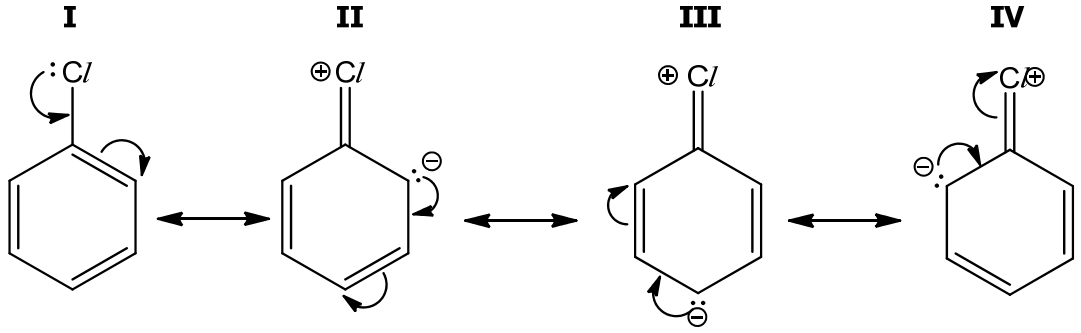
Using your answer in **(b)(ii)** and the above steps, suggest the complete mechanism by

- drawing curly arrows,
- showing lone pair(s) of electrons and
- identifying the slow step.

[3]



(c) Chlorobenzene has the following resonance structures which represent the alternative distribution of electrons on the molecule. Using these structures, suggest why the electrophilic substitution of chlorobenzene is 2,4-directing. [2]



The negative charges are located on positions 2 and 4 with respect to the chloro-group, hence the electrophilic attack is more likely to occur at these positions OR electrophile is more likely to react at these positions.

(d) When butane is reacted with chlorine gas under strong UV rays, a mixture of compounds is formed.

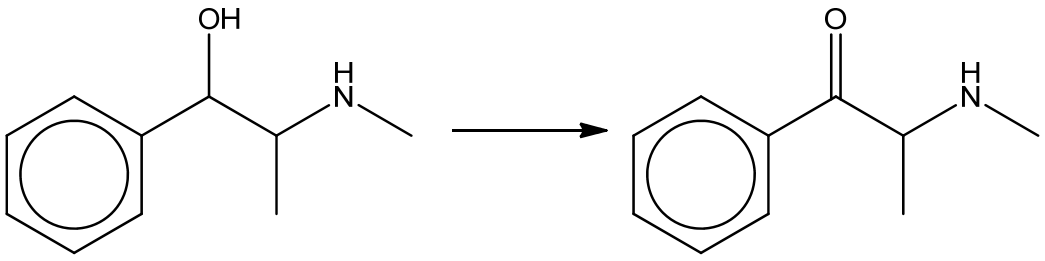
(i) Assuming that primary and secondary hydrogen atoms have similar reactivity, draw the structures of alkyl radicals formed during the reaction and state their likely ratio of formation. [2]

$CH_3CH_2CH_2\dot{C}H_2$ and $CH_3CH_2\dot{C}HCH_3$

3 : 2

		(ii)	During the termination stage, the alkyl radicals in **(d)(i)** form three structures with the molecular formula C_8H_{18}. Suggest their structures and the ratio of these structures. [4]
			• **$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_3$** **3/5 x 3/5 = 9/25** • **$CH_3CH_2CH(CH_3)CH(CH_3)CH_2CH_3$** **2/5 x 2/5 = 4/25** • **$CH_3CH_2CH_2CH_2CH(CH_3)CH_2CH_3$** **2 (3/5 x 2/5) = 12/25** • **Ratio = 9 : 4 : 12**
	(e)	Chlorofluoroalkanes, CFCs, were once used as refrigerant fluids and aerosol propellants. In many applications, they have now been replaced by alkanes. This is because CFCs contribute to the destruction of the ozone layer.	
		(i)	Suggest one reason why CFCs were originally used for this purpose. [1]
			CFCs have high heat capacity OR They are not easily flammable.
		(ii)	Suggest one potential hazard of using alkanes instead of CFCs. [1]
			Alkanes are flammable.
			[Total: 22]

2 Recreational drugs like methamphetamine and methcathinone can be synthesised easily from pseudoephedrine, a common nasal decongestant found in cough medicine.

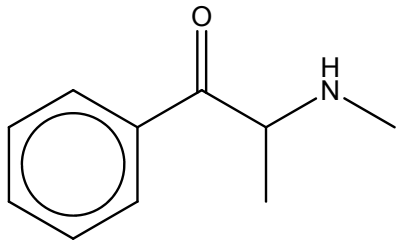
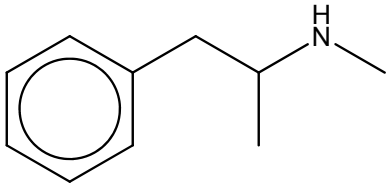


pseudophedrine methcathinone

HI, followed by neutralisation

X

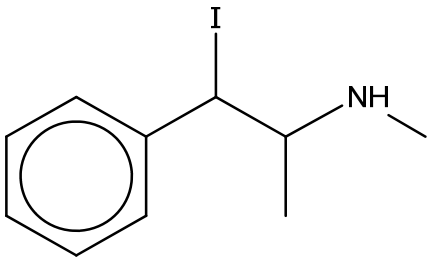
(a) (i) The structure of methcathinone and methamphetamine with pK_b values at 298 K, are shown in the table below.

compound	pK_b
 methcathinone	5.98
 methamphetamine	3.79

Explain why methcathinone has a higher pK_b value than methamphetamine. [2]

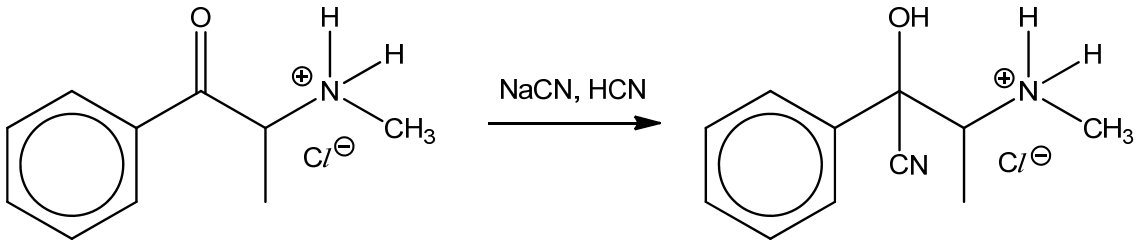
Methcathinone is a weaker base (higher pK_b) as it has a carbonyl (C=O) functional group two carbons away from secondary amine functional group, which is electron withdrawing. Hence the lone pair of electrons on N for methcathinone is less available for coordination with H^+ ion. (dative bonding with H^+ ion)

(ii) Suggest the structure of intermediate **X**. [1]



(b) Commercially, methcathinone is sold in its salt form as solid methcathinone hydrochloride.

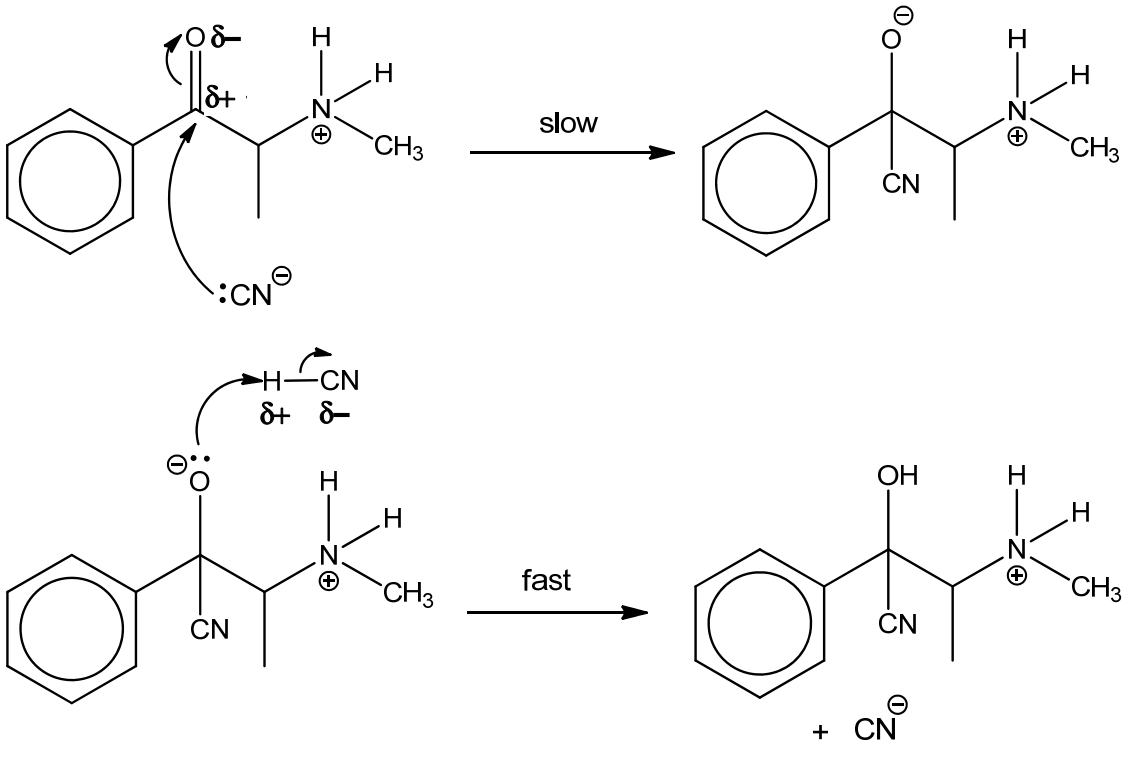
Methcathinone hydrochloride undergoes the following reaction to form a possible analogue, **Y**, with hallucinogenic properties.



methcathinone hydrochloride **Y**

Name the type of reaction and describe its mechanism, showing curly arrows, charges and any relevant lone pairs. [3]

Nucleophilic addition



(c) Hydrogen iodide, HI, is listed as a controlled substance as it is often used illegally to produce popular recreational drugs like methamphetamine.

The commercial preparation of hydrogen iodide, HI, involves the reaction of iodine I_2, with hydrazine, N_2H_4, which has ammonia-like properties.

$$N_2H_4(l) + 2I_2(aq) \longrightarrow N_2(g) + 4HI(g)$$

(i) During the preparation, gaseous hydrogen iodide produced must be removed immediately. Suggest a reason why this is done. [1]

Hydrazine N_2H_4 is basic and it can react with HI (acidic) to form a salt $N_2H_5^+I^-$

(ii) Hydrogen halides can be unstable to heat. Write an equation for the reaction undergone on heating hydrogen iodide, HI. [1]

$2HI \longrightarrow H_2 + I_2$

(iii) Using your knowledge of the chemistry of Group 17, deduce with reason how the thermal stability of hydrogen astatide, HAt, differ from that of hydrogen iodide, HI. [2]

At is below I in Group 17 so it forms weaker covalent bond with hydrogen. As a result, HAt has lower thermal stability than HI.

(d) A 40.0 g sample of solid ammonium carbonate is placed in a closed evacuated 3.0 dm^3 flask and heated to 400°C. It decomposes to produce ammonia, water and carbon dioxide according to the equation :

$$(NH_4)_2CO_3(s) \rightleftharpoons 2NH_3(g) + H_2O(g) + CO_2(g)$$

The value of the equilibrium constant, K_p, for the reaction is 0.295 at 400 °C.

In a gaseous reaction, the reactants and products can be expressed in partial pressures in atmospheres (atm). The relationship between K_c and K_p is given :

$$K_p = K_c(RT)^4$$

Assume that the gases are under ideal conditions.

(i) Write down the expression of K_p for the above equilibrium system. Hence show that $K_p = K_c(RT)^4$. [2]

$K_p = (P_{NH3})^2(P_{H2O})(P_{CO2})$

Using pV = nRT

P = (n/V)RT = CRT

$K_p = ([NH_3]RT)^2 ([H_2O]RT) ([CO_2]RT)$
$= [NH_3]^2 [H_2O][CO_2] (RT)^4$
$= K_c(RT)^4$

(ii) Calculate the partial pressure of $NH_3(g)$ at equilibrium at 400°C. [2]

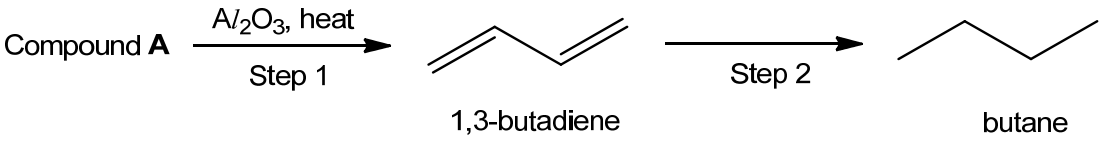
			$(NH_4)_2CO_3(s) \rightleftharpoons 2NH_3(g) + H_2O(g) + CO_2(g)$ I / atm 0 0 0 C / atm +2x +x +x E / atm 2x x x $K_p = (P_{NH3})^2(P_{H2O})(P_{CO2})$ $0.295 = (2x)^2(x)\ x)$ $x = 0.521$ $P_{NH3} = 2x = 1.04$ atm
		(iii)	Calculate the total pressure inside the flask at equilibrium. [1]
			$P_{total} = (P_{NH3}) + (P_{H2O}) + (P_{CO2})$ $= 2(0.521) + (0.521) + (0.521)$ $= 2.08$ atm
		(iv)	Calculate the mass of solid ammonium carbonate in the flask at equilibrium. [3]
			$PV = nRT$ $(0.521 \times 101325\ Pa)(0.003\ m^3) = n\ (8.31)(673\ K)$ $n = 0.02832$ mol Mass of $(NH_4)_2CO_3 = (40.0 - 0.02832)x(2(14.0) + 8(1.0) + 12.0 + 3(16.0))$ $= 37.3$ g
			[Total: 18]

3 In chemistry, a conjugated system refers to a system of overlapping p orbitals which allows the delocalisation of π electrons in a molecule. It is represented by having alternating single and multiple bonds in the molecule.

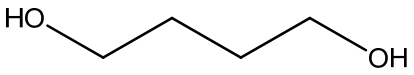
1,3-butadiene is the simplest conjugated diene which has double bonds that is separated by a single bond. It is a colourless gas which is industrially important as a monomer in the production of synthetic rubber.

In general, conjugated dienes have similar chemical properties as the usual alkenes. However, they are associated with extra stability as the delocalisation of π electrons lowers the overall energy of the molecule.

(a) The 2-step synthesis of butane shown in the figure below makes use of 1,3-butadiene as the intermediate.

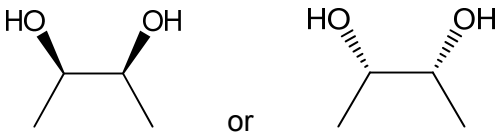


(i) Given that compound **A** does not rotate plane polarised light, suggest a structure for it and state the type of reaction that takes place in step 1. [2]

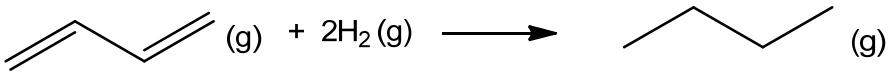


Elimination

Alternative answer:



(ii) Write an equation to show the standard enthalpy change of hydrogenation, $\Delta H^{\ominus}_{hydrogenation}$ of 1,3-butadiene in step 2. [1]

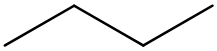


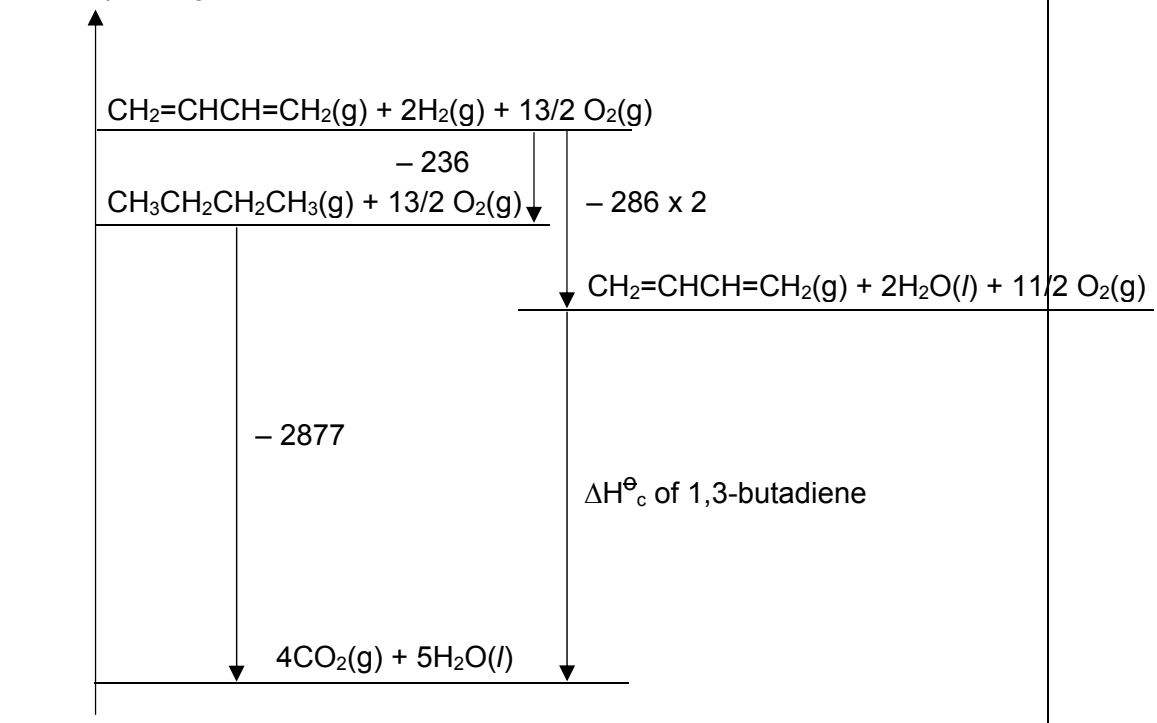
(iii) A student calculated the expected $\Delta H^{\ominus}_{hydrogenation}$ of 1,3-butadiene in step 2 to be –252 kJ mol^{-1}. However, 1,3-butadiene is 16 kJ mol^{-1} more stable than expected.

Calculate the actual $\Delta H^{\ominus}_{hydrogenation}$ of 1,3-butadiene. [1]

Actual $\Delta H^{\ominus}_{hydrogenation}$ of 1,3-butadiene = – 252 + 16 = –236 kJ mol^{-1}

(iv) Hence, using the value calculated in **(iii)** and the information given below, construct a fully labelled energy level diagram to determine the standard enthalpy change of combustion, $\Delta H^{\ominus}_c$ of 1,3-butadiene. [3]

substance	$\Delta H^{\ominus}_c$ / kJ mol^{-1}
	**–**2877
H_2	**–**286



$\Delta H^{\ominus}_c$ of 1,3-butadiene = – 2(–286) – 236 – 2877 = –2540 kJ mol^{-1}

(v) According to valence bond theory, the stability of conjugated diene could also be explained by orbital hybridisation.

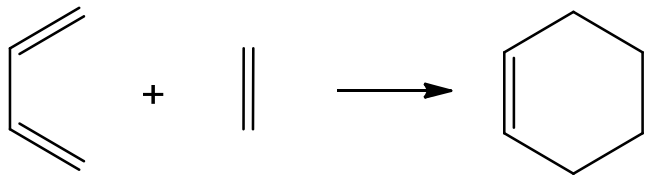
By making reference to the C–C single bond formed in 1,3-butadiene and butane, and the hybridisation of the orbitals in the two molecules, explain the extra stability of 1,3-butadiene. [2]

The C–C single bond in 1,3-butadiene are formed from the sigma overlap of sp^2 orbitals while the C–C single bond in butane are formed from the sigma overlap of sp^3 orbitals.

Since sp^2 orbital has more s character than sp^3 orbital, the electrons are sp^2 orbitals are closer to the nucleus, resulting in a stronger bond formed. Hence the extra stability of 1,3-butadiene results from the greater amount of s character in the orbital forming the stronger C–C single bond.

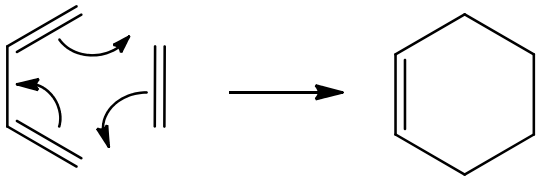
(b) Conjugate dienes can undergo addition with alkenes in a process called Diels-Alder reaction to form cyclic products. It is an important synthetic method which is widely used in organic chemistry to form unsaturated cyclic products.

An example of the Diels-Alder reaction is shown below where 1,3-butadiene reacts with ethene to form cyclohexene.:



In the process, the two reactants react in a single step through a cyclic redistribution of bonding electrons and two new carbon-carbon bonds are formed at the same time.

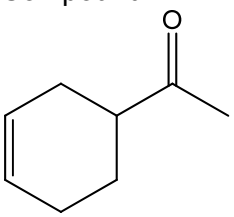
(i) By using full-headed curly arrows, suggest the mechanism that takes place in the above reaction to form cyclohexene. [1]

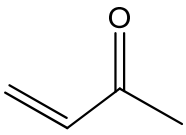


(ii) Compound **B** has the molecular formula of $C_8H_{12}O$ and it can be synthesised when 1,3-butadiene reacts with compound **C**, C_4H_6O, in the **Diels-Alder** reaction. It is known that compound **C** is able to react with 2 moles of hydrogen gas in the presence of Pt and produce a yellow precipitate with alkaline aqueous I_2. Compound **C** also gives a positive test with 2,4-dinitrophenylhydrazine and negative test with Tollens' reagent.

Suggest structures for compounds **B** and **C**, and explain the reactions described. [5]

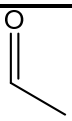
Compound **B**: Compound **C**:





[

	Deductions
Compound **B** can be synthesised when 1,3-butadiene reacts with compound **C**, C_4H_6O, in the **Diels-Alder** reaction.	• Compound **B** is a <u>cyclic</u> compound which contains an <u>alkene</u> functional group. • Compound **C** contains an <u>alkene</u> functional group which allows it to react with 1,3-butadiene.
Compound **C** is able to react with 2 moles of hydrogen gas in the presence of Pt and produce a yellow precipitate with alkaline aqueous I_2.	• Compound **C** undergoes <u>reduction</u> with 2 moles of hydrogen gas as it has <u>two unsaturated bonds / alkene and ketone functional group.</u>

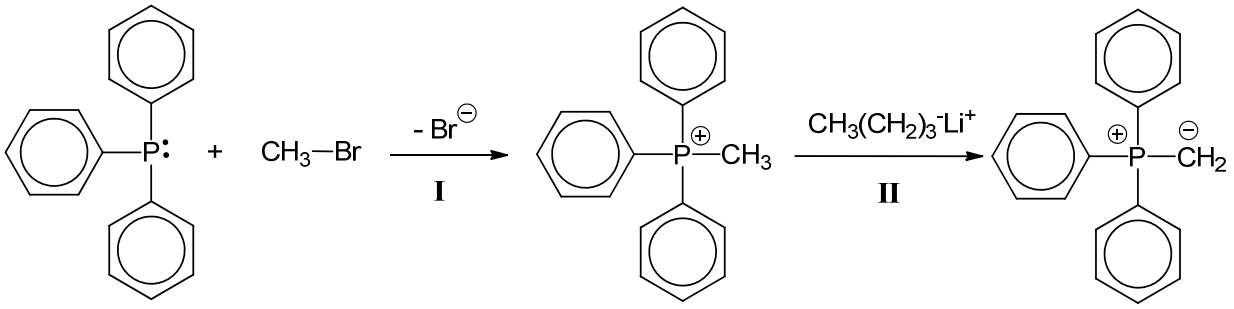
				• Compound **C** contains  group.	
			Compound **C** also gives a positive test with 2,4-dinitrophenylhydrazine and negative test for Tollens' reagent.	• Compound **C** undergoes <u>condensation</u> with 2,4-DNPH and it contains a <u>ketone</u> functional group.	
	(c)	Compounds of aluminium such as aluminium oxide, Al_2O_3 and aluminium chloride, $AlCl_3$ are often used in organic reactions as catalysts.			
		(i)	Aluminium oxide has unique chemical properties as it is able to react with both acid and base. Write balanced chemical equations for the reactions between aluminium oxide and the following respectively. • HBr • KOH [2] **$Al_2O_3(s) + 6HBr(aq) \longrightarrow 2AlBr_3(aq) + 3H_2O(l)$** **$Al_2O_3(s) + 2KOH(aq) + 3H_2O(l) \longrightarrow 2K[Al(OH)_4](aq)$**		
		(ii)	Account for the acid-base behaviour of aluminium oxide by making reference to its structure and bonding and state the nature of the oxide. [3] **Aluminium oxide has a giant ionic lattice structure with strong electrostatic forces of attraction between Al^{3+} and O^{2-} ions. However, due to the high charge density of the Al^{3+} ion, there is considerable covalent character in the compound, hence resulting it being an amphoteric oxide which can react with both acids and alkalis.**		

Section B

Answer **one** question from this section.

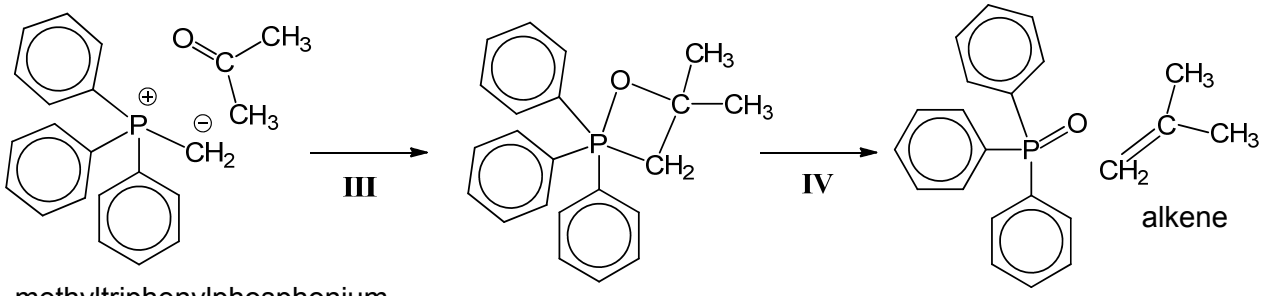
4 (a) The Wittig reaction converts carbonyl compounds into alkenes by reacting aldehydes or ketones with alkyltriphenylphosphonium, such as methyltriphenylphosphonium. During the reaction, the number of carbon atoms also increases.

Stage 1 – Preparation of methyltriphenylphosphonium



triphenylphosphine methyltriphenylphosphonium

Stage 2 – Formation of alkene



methyltriphenylphosphonium

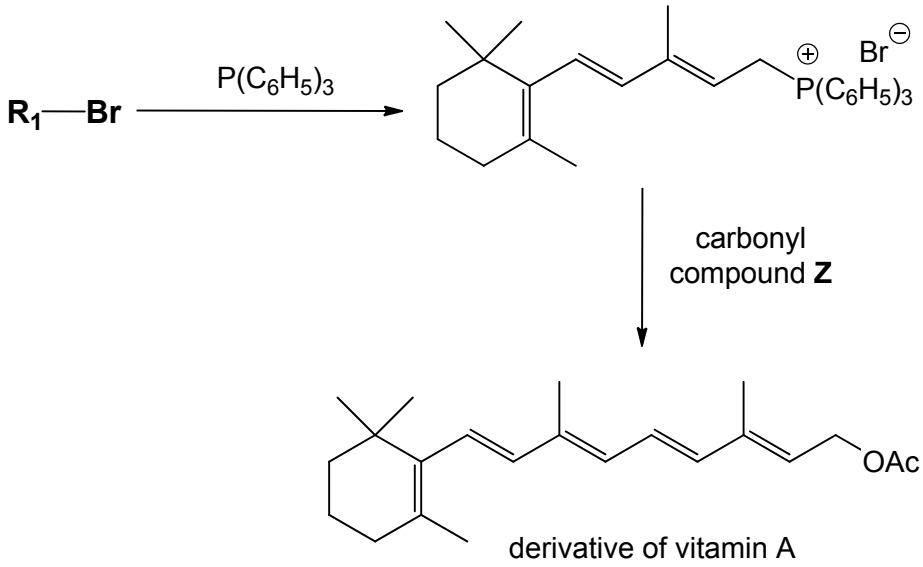
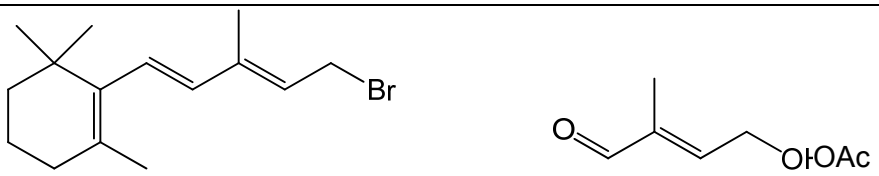
Different alkenes can be formed by using different carbonyl compounds and R-groups on the alkyltriphenylphosphonium.

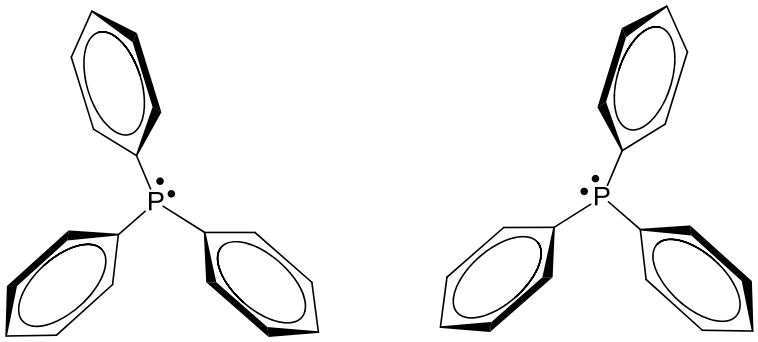
(i) The melting points of four compounds are given below.

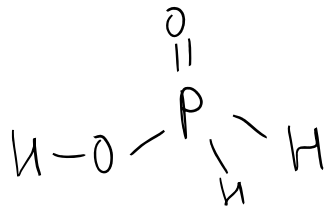
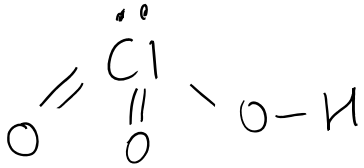
compound	*formula*	*melting point / °C*
triphenylphosphine	$P(C_6H_5)_3$	80
water	H_2O	0
methyltriphenylphosphonium bromide	$(C_6H_5)_3P{=}CH_2^+Br^-$	232
sodium chloride	NaC*l*	801

With reference to their structure and bonding, suggest why the melting point of

1. triphenylphosphine is higher than water; and
2. methyltriphenylphosphonium bromide is lower than sodium chloride [4]

			1. Both compounds have simple molecular structures with weak intermolecular forces of attraction between their molecules. Triphenylphosphine has larger and more polarizable electron cloud than water. Thus is has stronger instantaneous dipole-induced dipole interaction than (the hydrogen bonding of) water. **2. Both compounds have giant ionic lattice structures. Methyltriphenylphosphonium bromide has ions with larger radii than NaC*l*, hence lattice energy is less exothermic and melting point is lower.**
		(ii)	State the type of reaction in step **I**. [1]
			Nucleophilic substitution or S_N2
		(iii)	State the role of $CH_3(CH_2)_3^-Li^+$ in Step **II**. [1]
			Base
		(iv)	The advantage of Wittig reaction is the predictability of its alkene product. It is used in industrial processes such as the formation on vitamin A.  derivative of vitamin A Suggest the structures of alkylbromide **R_1–Br** and carbonyl compound **Z** for forming the derivative of vitamin A. You may assume that the OAc group remains unchanged during the reaction. [2]
			
	(b)	Triphenylphosphine, $P(C_6H_5)_3$, is prepared by reacting phosphorus trichloride, chlorobenzene and sodium. Sodium chloride is precipitated during the reaction due to its insolubility in the organic mixture.	
		(i)	Write the balanced equation for the preparation of triphenylphosphine. [1]
			$PCl_3 + 3C_6H_5Cl + 6Na \longrightarrow P(C_6H_5)_3 + 6NaCl$

		(ii)	Triphenylphosphine does not form in the above reaction when water is present. Given that phosphorus trichloride reacts with water according to the equation $PCl_3 + H_2O \longrightarrow H_3PO_3 + HCl$ describe, with the aid of equation(s), any other reactions that will take place when water is used as a solvent. Hence or otherwise, suggest the colour of universal indicator in the resulting mixture. [3]
			Using the mole ratio of PCl_3 and Na in the previous equation in (b)(i), **$6Na + 6H_2O \longrightarrow 6NaOH + 3H_2$** **$H_3PO_3 + 2NaOH \longrightarrow Na_2HPO_4 + H_2O$** **$HCl + NaOH \longrightarrow NaCl + H_2O$** **OR** **3 mol of NaOH is needed to completely react with 1 mol of H_3PO_3 and 1 mol of HCl.** **Due to the excess of NaOH, universal indicator shows a blue / violet colour.**
		(iii)	It has been suggested that triphenylphosphine is a chiral compound. Two structures of triphenylphosphine are shown below.  State the relationship of the two structures and suggest why triphenylphosphine is a chiral compound. [2]
			The two structures are enantiomers. **Triphenylphosphine has non-superimposable mirror images / no internal plane of symmetry.**
	(c)	**(i)**	The aqueous solutions of two acids were prepared and their pH measured. *acid* | *concentration / mol dm^{-3}* | *pH* **M** | 0.75 | 1.11 **N** | 0.25 | 0.60 Given that **M** and **N** are monobasic acids, show calculations to explain whether each acid is a strong or weak acid. [3]
			To determine if acid M dissociates fully: **–log(0.75) = 0.125** **Since pH is higher than 0.125, M did not dissociate fully. M is a weak acid.** **To determine if acid N dissociates fully:** **–log(0.25) = 0.60**

			Since pH is 0.60, N dissociated fully. N is a strong acid.
		(ii)	It is known that the electronegativity of the central atom in the acid affects its acidity. With reference to the increasing trend of electronegativity across the period, suggest the correct identities of the acids **M** and **N**, given that they could be H_3PO_2 or $HClO_3$. [3]
			M is H_3PO_2 and N is $HClO_3$.   **Cl atom is more electronegative than P , so it polarizes the O–H bond in $HClO_3$ to a greater extent, causing H^+ ion to be given off more readily, hence $HClO_3$ is a stronger acid, and must be N.** **OR** **Cl atom is more electronegative than P , so it disperses the negative charge on the conjugate base, ClO_3^-, to a greater extent. As the conjugate base is more stabilized, the acid is a stronger one.**
			[Total: 20]

5 *Use of the Data Booklet is relevant to this question*.

Osmium is a bluish-white metal found as a trace element in alloys, mostly in platinum ores. Not surprisingly, osmium was discovered in 1803 by Smithson Tennant when he noticed a residue remaining after dissolving crude platinum in aqua regia – a mixture of concentrated nitric acid and concentrated hydrochloric acid.

Platinum reacts with concentrated nitric acid to produce aqueous platinum(IV) cations, nitrogen dioxide and water. The platinum(IV) cations are then complexed with chloride *ligands* to produce hexachloroplatinate(IV) anions which are recovered through the reaction with ammonium chloride to produce yellow crystals.

(a) (i) Define the term *ligand*. [1]

A ligand is a neutral molecule or anion with at least one atom bearing a lone pair of electrons capable of dative bonding/coordinating to the central metal atom or ion.

(ii) Write a balanced ionic equation to represent the reaction of platinum with concentrated nitric acid. [1]

$Pt + 8HNO_3 \longrightarrow Pt^{4+} + 4NO_2 + 4NO_3^- + 4H_2O$

(iii) Suggest the identity of the yellow crystals obtained. [1]

$(NH_4)_2PtCl_6$

(iv) The solubility of the yellow crystals in water at room temperature is 5.0 g dm^{-3} but decreases to 0.028 g dm^{-3} in 1 mol dm^{-3} ammonium chloride at the same temperature.

Write an equation to represent the dissolution of the yellow crystals in in **(a)(iii)** and use the equation to account for the decreased solubility in 1 mol dm^{-3} ammonium chloride. [2]

$(NH_4)_2PtCl_6$ (s) ⇌ $2NH_4^+$ (aq) + $PtCl_6^{2-}$ (aq)

The solubility of the yellow crystals will be reduced as the position of equilibrium in the solubility equilibria is pushed back to the left due to the common ion effect brought about by NH_4^+.

(v) Explain why hexachloroplatinate(IV) is coloured. [3]

When chloride ligands approach the Pt^{4+} central cation, the degenerate d-orbitals/d-subshell split into two groups of different energy levels. An electron in the lower level can absorb energy equivalent to the energy gap which corresponds to a certain wavelength of light from the visible region of the electromagnetic spectrum and be promoted to the higher energy level. The colour seen is complementary to the colour absorbed.

When powdered osmium is exposed to air, it forms the toxic compound osmium tetroxide, OsO_4 with a strong odour like that of chlorine.

$$Os + 2O_2 \longrightarrow OsO_4$$

(b) (i) Use the standard electrode potential given and choose another appropriate equation from the *Data Booklet* to calculate the $E^{\ominus}_{cell}$ for the reaction between osmium and air. [1]

$$OsO_4 + 8H^+ + 8e^- \rightleftharpoons Os + 4H_2O \qquad E^{\ominus} = +0.84\ V$$

Choose $O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O$ $\quad E^{\ominus} = +1.23$ V

$E^{\ominus}_{cell} = E^{\ominus}_{cathode} - E^{\ominus}_{anode}$
$= +1.23 - (+0.84)$
$= +0.39$ V

(ii) Hence calculate $\Delta G^{\ominus}_{cell}$ for the reaction in **(b)(i)**, leaving your answer in kJ mol^{-1}. [1]

$\Delta G^{\ominus}_{cell} = -nFE^{\ominus}_{cell}$
$= -(8)(96500)(+0.39)$
$= -301\ 080$ J mol^{-1}
$= -301$ kJ mol^{-1}

(iii) Suggest, with reasoning, the sign for the standard enthalpy change of reaction for the reaction between osmium and air, making reference to the terms in the Gibbs free energy equation and your answer in **(b)(ii)**. [2]

Since the standard entropy change is negative due to the decrease in number of moles of gaseous oxygen/loss of oxygen, the standard enthalpy change of reaction must be negative too for $\Delta G^{\ominus}_{cell}$ to be overall negative.

The figure below shows part of a label on a bottle of osmium tetroxide.

Osmium Tetroxide, OsO_4

Molar mass: 254.2 g mol^{-1}
Density: 4.9 g cm^{-3}
Vapour pressure: 933 Pa
Max. permissible exposure limit: 200 μg m^{-3}

Net weight: 1000 g
Volume of container: 250 cm^3

Note:
Vapour pressure – the pressure of vapour in equilibrium with its solid/liquid form.
1 μg = 1 x 10^{-6} g

(c) (i) Use the information above to calculate the amount of OsO_4 in the vapour phase within an unopened container of OsO_4 at room temperature. Assume ideal gas behaviour. [2]

Gas volume = $250 - \frac{1000}{4.9} = 45.9\ cm^3$

$n(OsO_4\ vapour) = \frac{pV}{RT} = \frac{933 \times \frac{45.9}{1\,000\,000}}{8.31 \times 293} = 1.76 \times 10^{-5}$ mol

(ii) Hence determine the concentration of OsO_4, in μg m^{-3}, in the air of a 100 m^3 laboratory where a new container is opened. Assume that the air has evenly mixed.

[2]

$m(OsO_4\ vapour) = 1.76 \times 10^{-5} \times 254.2 = 4.47 \times 10^{-3}$ g

$[OsO_4] = \frac{4.47 \times 10^{-3}}{100} = 4.47 \times 10^{-5}$ g m^{-3} = 44.7 μg m^{-3}

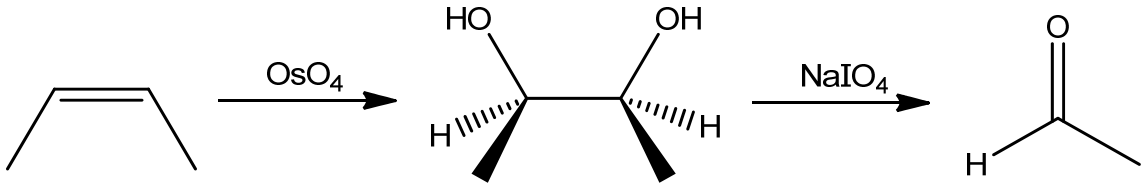
(iii) Discuss whether it is safe for researchers to open the container in this laboratory without a proper fume cupboard, considering your answer in **(c)(ii)** and the approach used to calculate it. [1]

Yes, since the effective concentration of 44.7 μg m^{-3} is less than the maximum permissible exposure limit of 200 μg m^{-3}.

OR

No, it is not safe as the vapour takes time to diffuse evenly throughout the room. The immediate air around the researchers will have a concentration of OsO_4 exceeding the maximum permissible limit.

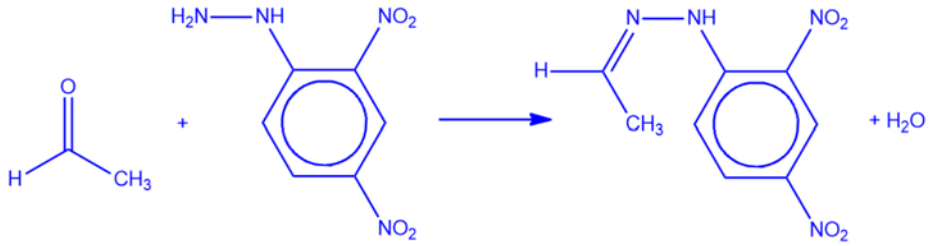
Osmium tetroxide, OsO_4 can oxidise alkenes to give diols. $NaIO_4$ will react further with the diol to produce carbonyl compounds.



A **B**

(d) Suggest a simple chemical test to distinguish between compounds **A** and **B** and write a balanced equation for the positive test. [3]

2,4-DNPH, room conditions
Yellow crystals formed with **B** but no yellow crystals formed with **A**.



OR

Tollens' reagent, warm
Silver mirror formed with **B** but no silver mirror formed with **A**.
$CH_3CHO + 2[Ag(NH_3)_2]^+ + 3OH^- \longrightarrow 2Ag + 4NH_3 + CH_3CO_2^- + 2H_2O$

OR

Fehling's reagent, warm
Red-brown ppt formed with **B** but no red-brown ppt formed with **A**.
$CH_3CHO + 2Cu^{2+} + 5OH^- \longrightarrow CH_3CO_2^- + Cu_2O + 3H_2O$

OR

Sodium, room conditions
Effervescence observed with **A**. Gas evolved extinguishes lighted splint with a pop sound. No effervescence observed with **B**.

OR

PCl_5, room conditions
Steamy/White fumes observed with **A** but no white fumes observed with **B**.
$CH_2(OH)CH_2OH + 2PCl_5 \longrightarrow CH_2ClCH_2Cl + 2POCl_3 + 2HCl$

OR

$SOCl_2$ (pyridine), heat
Steamy/White fumes observed with **A** but no white fumes observed with **B**.
$CH_2(OH)CH_2OH + 2SOCl_2 \longrightarrow CH_2ClCH_2Cl + 2HCl + 2SO_2$

[Total: 20]

– End of Paper –