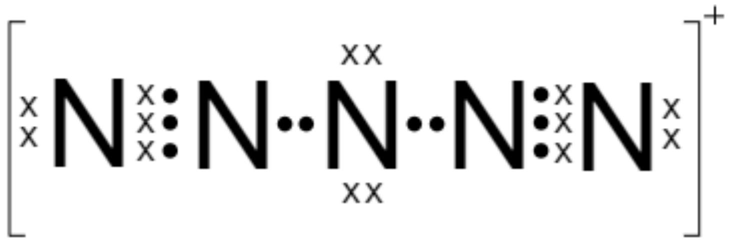
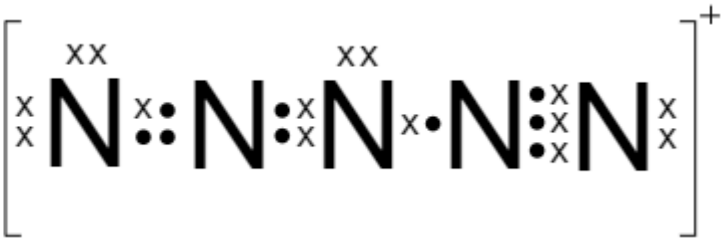
Qn.		**Suggested Solutions**	**Remarks**
1 (a)	**(i)**	The VSEPR theory states that: • Electron pairs arrange themselves in a way to minimise electron pair-electron pair repulsion [1] • Repulsion between electron pairs is arranged from the strongest to weakest as follows: lone pair-lone pair, bond pair-lone pair, bond pair-bond pair [1]	
	(ii)	N_b and N_d: linear N_c: bent [1] for all correct; no marks otherwise	Candidates are required to deduce that 168° is close to linear geometry.
	(iii)	[2] for either of the structures: Structure **A**  Structure **B** (accept its mirror image)  Marking points: [1] for ensuring that N_a—N_b and N_d—N_e bond has a bond order that is higher than (or at least equal to) the N_b—N_c and N_c—N_d bond. The former bond length is shorter than the latter. For structure **A**: the bond order for N_a—N_b and N_d—N_e is 3 (triple bond), while that of N_b—N_c and N_c—N_d is 1. For structure **B**: the bond order for N_a—N_b and N_b—N_c is 2, N_c—N_d is 1, and N_d—N_e is 3.	

[1] for ensuring that the geometry at N_b and N_d is linear (i.e. no lone pairs on N_b and N_d), and N_c is bent (1 or 2 lone pairs)

No other resonance structures will be accepted.

(iv) If structure **A** is drawn, N_c has an oxidation state of +1, while N_a, N_b, N_d and N_e has an oxidation state of 0. [1]

If structure **B** is drawn, N_b has an oxidation state of +1, while N_a, N_c, N_d and N_e has an oxidation state of 0. [1]

- If the candidate states that N_d has an oxidation state of +1, this is acceptable as long as the oxidation state of N_b is stated to be 0.

(b) **(i)** $[N_5^+][N_3^-] \rightarrow 4\ N_2$ [1]

Accept equations including spectator ions Cs^+ and SbF_6^-, as long as the equation is balanced AND nitrogen gas is one of the products.

(ii) The oppositely charged poly-nitrogen species attract each other once its salt dissolved in liquid SO_2, which is a kinetically feasible reaction making this reaction fast and uncontrollable. [1]

(iii) Identifies $CsSbF_6$ AND amount of $CsSbF_6$ = 0.002438 mol [1], accept 3 s.f. value

An excess was produced. [1] (This is because some liquid SO_2 was present too.)

(iv) $[Cs^+] = [N_3^-] = 3.14\ \text{mol dm}^{-3}$ [1]

[1] for final answer with working

$$\text{Volume of } SO_2 = \frac{2.267\times10^{-3}}{3.14} = 7.22\times10^{-4}\ \text{dm}^3$$

(v) Lowers the solubility because Cs^+ present will lower amount of $CsSbF_6$ needed to be dissolved to achieve $[Cs^+][SbF_6^-] = K_{sp}$. [1]

Accept answers based on discussing the equilibrium:

$$CsSbF_6 \rightleftharpoons Cs^+ + SbF_6^-$$

Presence of Cs^+ shifts the position of equilibrium to the left so less $CsSbF_6$ dissolves.

(c) **(i)** [1] for calculating volume of the covering (with correct units indicated)

$$V = \pi\left(\frac{7.00\times10^{-3}}{2}\right)^2 \times 45.0\times10^{-3} = 1.7318\times10^{-6}\ \text{m}^3$$

The candidate is expected to know the

volume of a cylinder.

[1] calculates amount of N_2 produced

$$n_{N_2} = \frac{0.600}{207.2 + 14.0 \times 6} \times \frac{6}{2} = 0.0061813 \text{ mol}$$

[1] Establishes relationship pV = nRT and solves for p.

The candidate may assume the temperature to be a reasonable one. For example, T = 293 K (room temperature), or T = 298 K (standard conditions), or T = 273 K (standard temperature). The candidate may choose to assume a high temperature since energy is applied for the decomposition.

Taking T = 293 K,

$$p = \frac{nRT}{V} = \frac{0.0061813 \times 8.31 \times 293}{1.7318 \times 10^{-6}} = 8.69 \times 10^{6} \text{ Pa}$$

(Note: This pressure is enough to blow off your hand if you held the detonator in your hand.)

Only ecf for the 3rd marking point is awarded.

(ii) High charge density of Fe^{3+} centre polarises/weakens the O—H bond on the H_2O ligand. [1]

(iii) Different ligand results in different splitting parameter (or energy gap). So light of a different colour is absorbed and its complementary colour transmitted is different. [1]

(iv) [1] correct expression for K_c (no approximation should be done)
[1] correct substitution of values leading to $[N_3^-]$

$$\frac{1.40 \times 10^{-6}}{\left(0.0200 - 1.40 \times 10^{-6}\right)\left(10^{-2.72}\right)[N_3^-]} = 0.5088$$

$[N_3^-]$ = 0.072207 mol dm^{-3} (candidates that did not read that a buffer was used would obtain the value 0.0722604 mol dm^{-3}, penalise 1 mark)

[1] for calculating amount N_3^-
[1] for calculating mass of $Cu(N_3)_2$

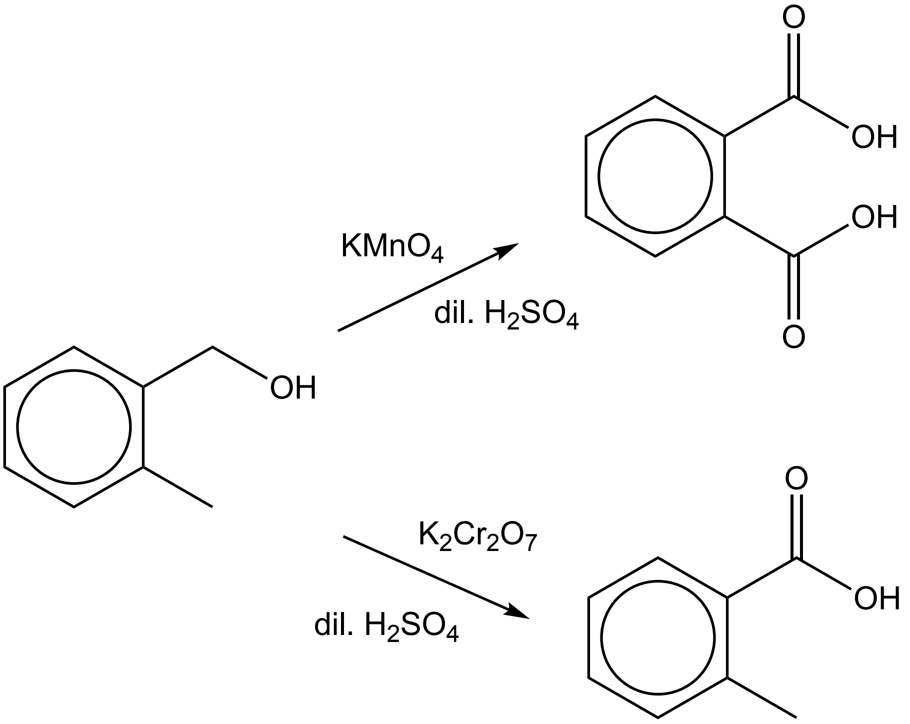
Candidates are reminded to leave intermediate values to 4 to 5 significant figures. Failure to do so will result in s.f. penalty or truncation errors.

Since the amount of free N_3^- is much more that in the iron(III) complex, we can ignore the amount of N_3^- in the iron(III) complex. (If the candidate takes into account of the N_3^- in the iron(III) complex, it is also acceptable. This method is only done because it simplifies the calculations by a bit.)

Amount of N_3^- = $0.072207 \times \frac{5.00}{1000}$ = 0.000361035 mol

Mass of $Cu(N_3)_2$ = $0.000361035 \times \frac{63.5 + 14.0 \times 6}{2}$ = 0.0266 g (3 s.f.)

2 **(a)** [1] for correct reaction with $KMnO_4$
[1] for correct reaction with $K_2Cr_2O_7$
[1] for explanation that a side reaction occurred with $KMnO_4$



A chemist may want to convert the starting product to the bottom one on the right. Using $KMnO_4$ will result in side-chain oxidation occurring too which produces the unintended product on top.

(b) **(i)** Immediate distillation [1]

(ii) $R\text{—}CH_2OH \rightarrow 2\ e^- + R\text{—}CHO + 2\ H^+$ [1]

Ignore state symbols

(iii) To separate samples of **A** and **B**, add PCC at room temperature

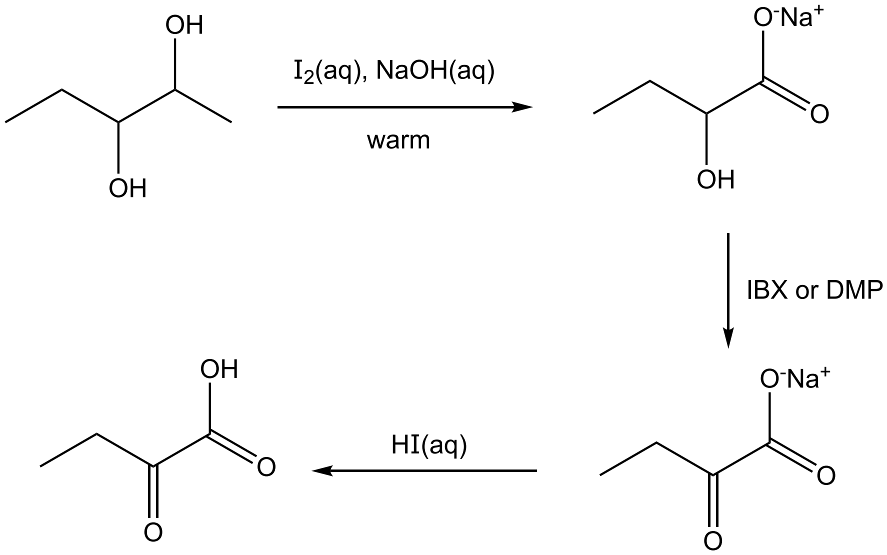
The following combinations of tests are accepted:

Then add Tollen's reagent (and warm) [1]
No silver mirror is formed for **A**. [1]
Silver mirror is formed for **B**. [1]

Then add Fehling's reagent (and warm) [1]
No precipitate is formed for **A**. [1]
Brick red precipitate is formed for **B**. [1]

Then add I_2(aq), NaOH(aq) (and warm) [1]
Yellow precipitate is formed for **A**. [1]
No precipitate is formed for **B**. [1]

(c) **(i)**



[1] for each correct step
[1] for each correct intermediate

No ecf is awarded.

For the 3rd step, accept any (rather strong) iodine containing acids like: HIO_3, HIO_4.
Credit for an intermediate and its previous step will be voided if DMP and IBX is used.

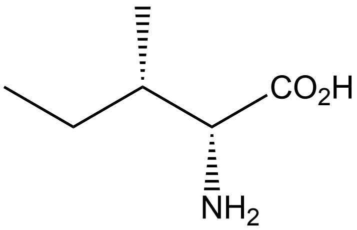
Alternative answer:
[1] excess DMP
[1] correct intermediate
(Note: either of the 2 alcohol groups will be oxidised. If the C3 alcohol group is NOT oxidised, then DMP must be added again. To guarantee the C3 alcohol group to be oxidised, DMP should be in excess. The word excess should be present to score credit for the first point. Alternatively, the candidate include an additional step where DMP is use to guarantee the oxidation of the alcohol to a ketone.)
[1] I_2(aq), NaOH(aq), warm/heat
[1] correct intermediate (second last intermediate in answer)
[1] iodine-containing acid

(ii) Oxidation state of iodine in both IBX and DMP is +3. [1]

Geometry of iodine in IBX: See-saw
Geometry of iodine in DMP: Square pyramidal
[1] for both correct

3 (a) (i) An atom that has four different groups/ligands attached to it (in tetrahedral configuration). [1]

(ii) [1] correct structure of **B**



Different melting point AND rotates plane polarised light to a different extent when compared to **A**. [1]

(iii) $2^6 = \underline{64}$ stereoisomers [1]

(iv) **A** and **B** are not enantiomers of each other [1] since only one of the chiral carbons has a different stereochemical configuration.

(b) (i) First order because the rate constant has units in the dimension of time inverse. [1]

Candidates are expected to write an explanation and deduce the answer based on the dimensions of *k*.

(ii) 0 J mol^{-1}. **R** and **S** have same physical properties so their Gibbs' Free Energy of formation must be the same. [1]

(iii) H_2SO_4(aq), heat with reflux (any strong acid is acceptable)
OR
NaOH(aq), heat with reflux (any strong alkali is acceptable) [1]

(iv) Since [**R**] = 0 mol dm^{-3} before the hydrolysis when $t = 0$ s,

$$\ln\left(\frac{[\mathbf{S}]}{[\mathbf{S}]}\right) = 2k(0) + C$$

A convincing explanation must be offered.

So C = 0. [1]

(v) [1] for substitution of [**R**] = 0.059[**S**] into the expression

$$\ln\left(\frac{[\mathbf{S}] + 0.059[\mathbf{S}]}{[\mathbf{S}] - 0.059[\mathbf{S}]}\right) = 2(4\times60^2)k_2$$

$k_2 = 4.102 \times 10^{-6}\ \mathrm{s}^{-1}$ [1] (correct value in SI units)

(vi) [1] for substitution of [**R**] = 0.090[**S**] into the expression to find C, when the second racemisation process (after the boiling of the body), has taken place.

$$\ln\left(\frac{[\mathbf{S}] + 0.090[\mathbf{S}]}{[\mathbf{S}] - 0.090[\mathbf{S}]}\right) = 2\left(4\times60^2\right)\left(4.102\times10^{-6}\right) + \mathrm{C}$$

$\mathrm{C} = 6.235 \times 10^{-2}$

[1] for finding the [**R**] to [**S**] ratio before the start of the hydrolysis and after the body was boiled

Let $\frac{[\mathbf{R}]}{[\mathbf{S}]} = x$.

$$\ln\left(\frac{[\mathbf{S}] + x[\mathbf{S}]}{[\mathbf{S}] - x[\mathbf{S}]}\right) = 2(0)\left(4.102\times10^{-6}\right) + 6.235 \times 10^{-2}$$

$$\ln\left(\frac{1 + x}{1 - \mathrm{x}}\right) = 6.235\times10^{-2}$$

$x = 0.03115$

[1] for final answer through substitution of expression

$$\ln\left(\frac{[\mathbf{S}] + 0.03115[\mathbf{S}]}{[\mathbf{S}] - 0.03115[\mathbf{S}]}\right) = 2(t)(1.417\times10^{-6})$$

$t = 2.20 \times 10^4$ seconds (approximately 6 hours)

(c) If the body was boiled, the liver sample will not decompose the hydrogen peroxide. No brisk effervescence will be observed.

If the body was not boiled, the liver sample will catalyse the decomposition of the hydrogen peroxide. Brisk effervescence will be observed. [1]

The enzyme will denature during boiling, so it cannot perform its function of catalysis anymore. [1]

(d) **(i)** [1] for amount of water

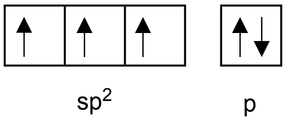
$$n_{H_2O} = n_{I_2} = \frac{5.027\times10^{-3}}{2} = 2.5135\times10^{-3}\text{ mol}$$

[1] for percentage composition of water by mass with working

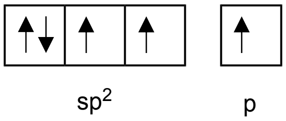
$$\%\text{ water} = \frac{2.5135\times10^{-3}\times(16.0+2\times1.0)}{5.203}\times100\% = 0.870\%$$

(ii) Bronsted-Lowry base as Im accepts a proton to form the ImH^+ ion. [1]

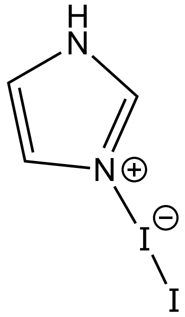
(iii) For the N atom bonded to the H: [1]



For the N atom not bonded to the H: [1]



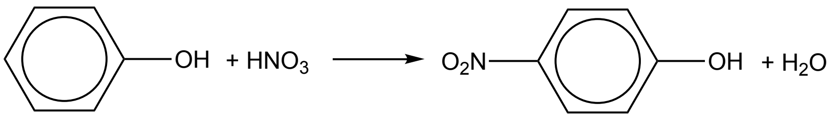
(iv) N atom not bonded to the H because the lone pair resides in the sp^2 orbital, so it is a localised lone pair. N atom bonded to the H has its lone pair delocalised (thereby needing it to reside in the p orbital). [1]



[1] (usage of → for dative bonding is acceptable)

4 **(a)** **(i)** dilute nitric acid at room temperature [1]

(ii)



[1] balanced equation must include water

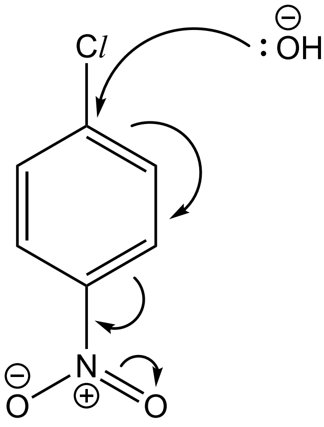
(iii) Presence of intramolecular hydrogen bonding in 2-nitrophenol results in a lower boiling point than 4-nitrophenol. [1]

(b) **(i)** The C—C*l* bond has partial double bond character as the lone pair on C*l* can delocalise into the benzene ring. The C—C*l* bond is hence harder to break. [1]

Steric hinderance from the electron-cloud of the benzene ring causes the repulsion of the OH^- nucleophile, thus making the nucleophilic attack energetically unfeasible. [1]

(ii) Nitrate chlorobenzene since the C*l* group is 2,4 directing, while the nitro group is only 3 directing. [1]

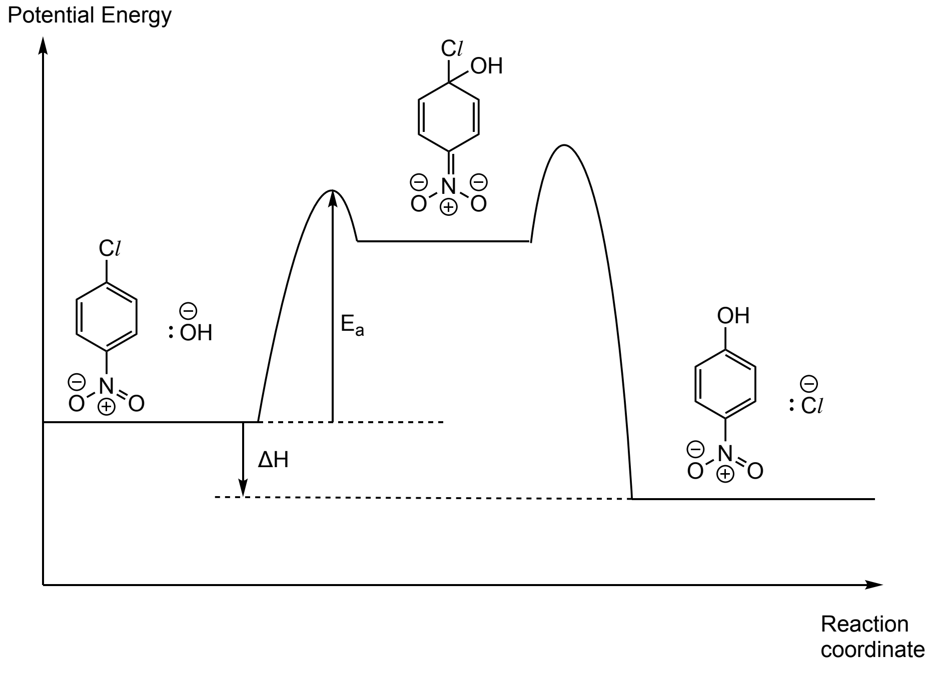
(iii)



[1]

(iv) This will not work. The pi-electrons can only be directed to the 2 or 4 position (with respect to the chlorine) [1] because at the 3 position, there are no pi-electrons available to be pushed to the nitro-group at the 3 position, instead the pi electrons will end up on another C—C bond. [1]

(v)



[1] for correct reactants, intermediates and products (they need to be balanced in terms of material and charge)
[1] for labelling ΔH of overall equation and E_a of step 1. E_a of step 1 must be larger than E_a of step 2.
[1] for labelling axes
ΔH < 0 is not mandatory, but is preferred in the answer.

(c) **(i)**

X	ΔH / kJ mol^{-1}
F	-479
C*l*	-117
I	+22

[1] for 1 correct with working
[1] for all others correct

If no working is offered,
[2] for all correct, [1] for 2 correct

(ii) The iodination of benzene is endothermic, while the chlorination of benzene is exothermic. It is not so energetically favourable to iodinate benzene, while it is overall, energetically feasible to do so to chlorinate benzene since energy is released. [1]

(iii) +4. 2 moles of electrons are lost by 1 mole of I_2, so 1 mole of electron is gained per mole of HNO_3. [1]

(iv) $I_2 + 2\ HNO_3 \rightarrow 2\ NO_2 + 2\ I^+ + H_2O$ [1]

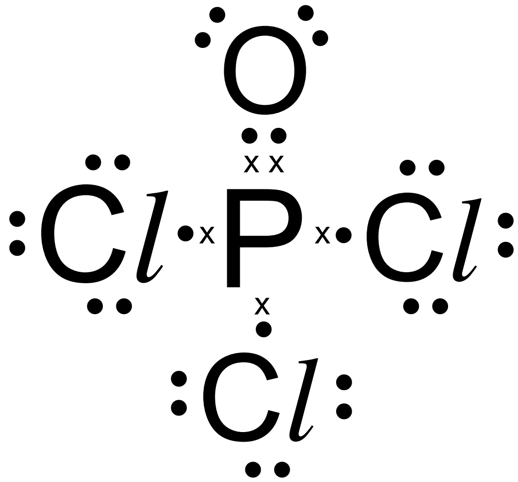
(v) F^- ion has a smaller radius and less electrons than the Cl^- ion. Hence the electron cloud in F^- is less polarisable than that of the Cl^- ion. [1]
The Al^{3+} ion is unable to polarise the F^- ion to the extent where its electron cloud can overlap with the Al^{3+} ion, but the Al^{3+} ion can polarise the electron cloud of the Cl^- ion to the extent where its electron could can overlap with the Al^{3+} ion. [1]

5 **(a)** **(i)** $P_4 + 5\ O_2 \rightarrow P_4O_{10}$ [1]
$P_4O_{10} + 6\ H_2O \rightarrow 4\ H_3PO_4$ [1]

(ii) $NaHCO_3$ can act as a Bronsted-base to neutralise the phosphoric acid. [1]

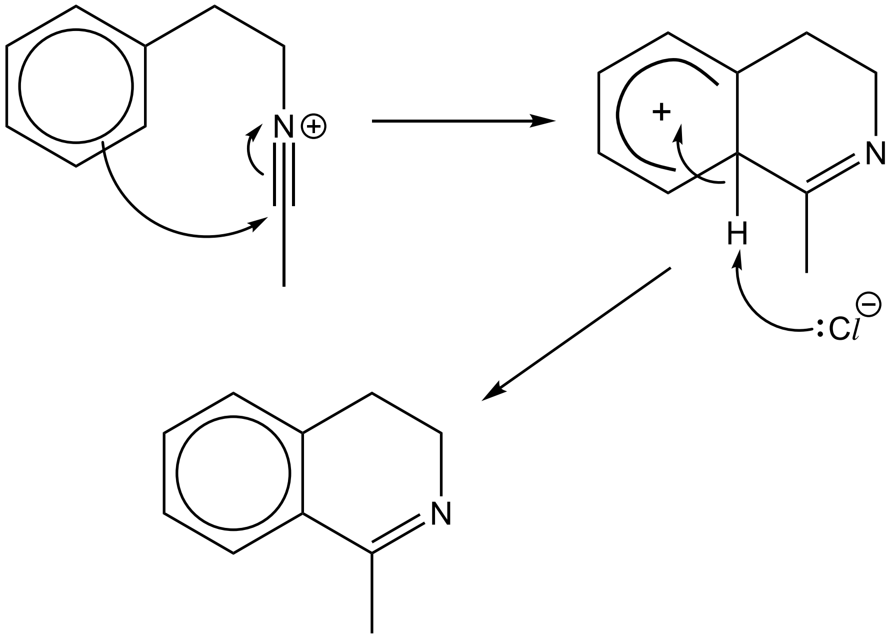
(iii) The immersion of the affected ammunition in water cuts the exposure to oxygen, thereby preventing further combustion. [1]

(b) **(i)**



[1]

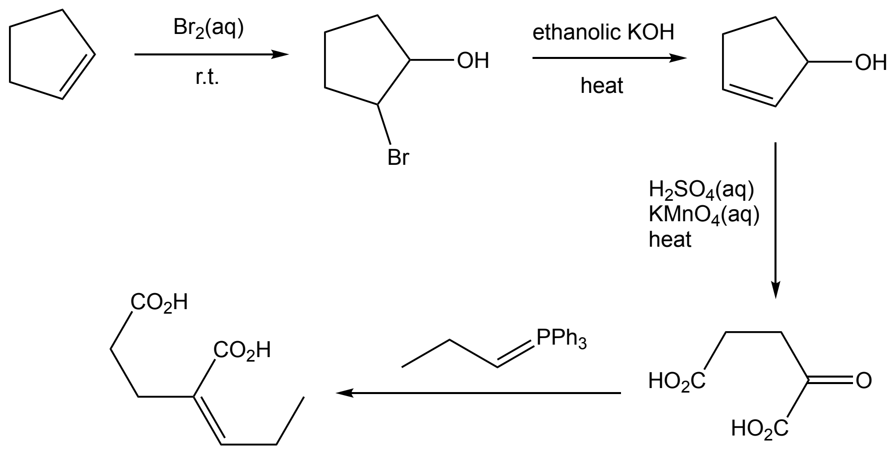
(ii)



[1] for each step
Each step must have curly arrows and charges illustrated.
Slow step is not needed since the full mechanism is not shown.

(iii) Dehydration OR Elimination [1]

(c) **(i)**



[1] each for each step
[1] each for each intermediate

(ii) Condensation [1]

(d) **(i)** [1] for both correct answers

Without oxygen: 2.15%
With oxygen: 40.9%

(ii) The entropy change is negative because the folding of the protein causes the system to become much more ordered, as compared to many free amino acid molecules. [1]

Focus on the words “specific” and “restricted”

(iii) Amount of peptide links = $\frac{10^{20}\times150}{6.02\times10^{23}}$ = 2.4917×10^{-2} mol [1]

Amount of ATP = $\frac{2.4917\times10^{-2}\times17}{31}$ = 1.3664×10^{-2} mol

Amount of glucose = $\frac{1.3664\times10^{-2}}{40.9\%}$ = 3.34×10^{-2} mol [1]