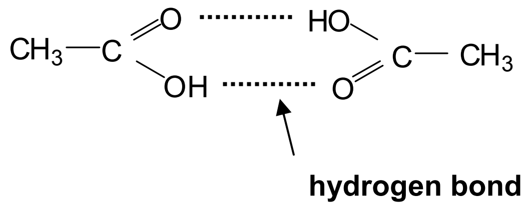
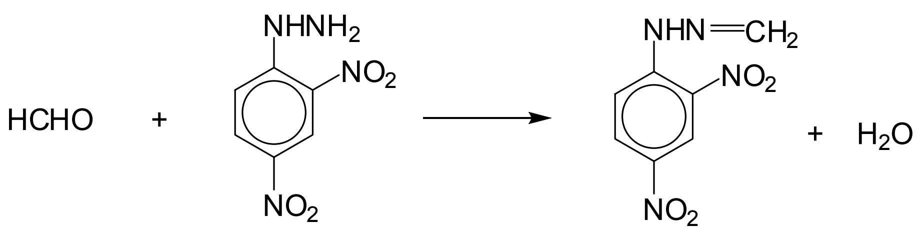
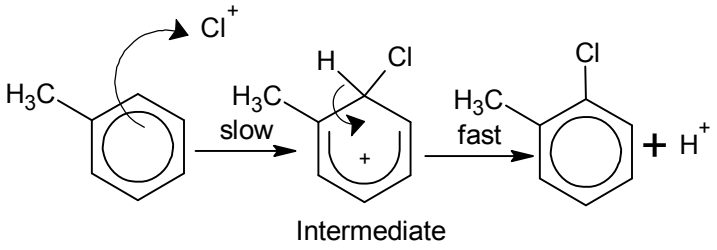
2008 H2 Chemistry Preliminary Examination Paper 3 Mark Scheme

1	**(a)(i)**	<u>Order of rxn wrt to Br_2</u> Comparing expt 1 & 3, when $[Br_2]$ triples from 0.01 to 0.03 moldm^{-3}, the rate of rxn also triples. Hence, $[Br_2]$ is directly proportional to the rate of rxn. Order of rxn wrt Br_2 = 1 <u>Order of rxn wrt to HCOOH</u> Comparing expt 1 & 2, $\frac{8.0 \times 10^{-6}}{2.0 \times 10^{-6}} = \frac{(0.02)^1(0.04)^x}{(0.01)^1(0.02)^x}$ x = 1 Order of rxn wrt HCOOH = 1 * can used any 2 sets of expts to compare too. **Rate = k$[Br_2]$[HCOOH]**
	(a)(ii)	6.0×10^{-6} = k (0.03) (0.02) k = **0.01 mol^{-1} dm^3 s^{-1}**
	(a)(iii)	The reaction involves **1 mole of Br_2 and 1 mole of HCOOH in the rate determining step**. Overall, this is a **one-step reaction**.
	(a)(iv)	After mixing, $[Br_2]$ = 0.005 mol dm^{-3} [HCOOH] = 0.01 mol dm^{-3} Rate = (0.01)(0.005)(0.01) **= 5.0 x 10^{-7} mol dm^{-3} s^{-1}**
1	**(b)(i)**	Methanal, methanol and methanoic acid are all **polar molecules** and exist as **simple molecular structure**. Methanal has **permanent dipole-permanent dipole** interaction between molecules. Methanol and methanoic acid have **hydrogen bonds** between molecules. Since **permanent dipole-permanent dipole is weaker than hydrogen bonds**, less energy is needed to over the attractions between methanal. Hence, methanal has the lowest boiling point. Methanoic acid forms **more extensive hydrogen bonds** than methanol.

		Thus, more energy is needed to overcome the attractions between methanoic acid. Hence, boiling point of methanoic acid is higher than that of methanol. [Generally, compare: *difference between methanal and ‘methanol and methanoic acid’ *difference between methanol and methanoic acid]
	(b)(ii)	In benzene solution, methanoic acid **dimerises through hydrogen bonds.** 
	(c)(i)	**(1) 2,4-DNPH, at room temp** - methanal ⇒ orange ppt - methanoic acid ⇒ no orange ppt  **(2) Na_2CO_3(aq), room temp** - methanal ⇒ no CO_2(g) - methanoic acid ⇒ CO_2(g) evolved which forms white ppt with $Ca(OH)_2$ (aq) $2\ HCOOH + Na_2CO_3\ (aq) \longrightarrow 2\ HCOONa + CO_2 + H_2O$
1	**(c)(i) con’t**	**(3) Na(s), room temp** - methanal ⇒ no H_2(g) - methanoic acid ⇒ H_2(g) which gives a ‘pop’ sound with lighted splinter $HCOOH + Na\ (s) \longrightarrow HCOO^-Na^+ + \frac{1}{2} H_2\ (g)$
	(c)(ii)	**(1) $KMnO_4/H^+$, heat** - methanoic acid ⇒ decolourise purple $KMnO_4$ and give CO_2(g) which forms white ppt with limewater. - ethanoic acid ⇒ no decolourisation of purple $KMnO_4$ $HCOOH + [O] \longrightarrow CO_2 + H_2O$ **(2) aq. silver nitrate in excess ammonia solution, warm**

		- methanoic acid $\Rightarrow$ silver mirror - ethanoic acid $\Rightarrow$ no silver mirror $HCOOH + 2[Ag(NH_3)_2]^+ + 2\ OH^- \rightarrow (NH_4)_2CO_3 + 2\ Ag + 2\ NH_3 + H_2O$ *Reagent and conditions [1] *Observations(+ve and –ve) [1] *Balanced equations [1]

2	**(a)(i)**	Standard electrode potential is defined as the potential difference between a standard hydrogen electrode and an electrode immersed in a solution containing ions at 1 mol dm^{-3} concentration at 25°C and 1 atmospheric pressure
	(a)(ii)	E^{θ}_{cell} = +0.77 – 0.34 = **+0.43 V**
	(a)(iii)	$Cu \rightarrow Cu^{2+} + 2e$ $Fe^{3+} + e \rightarrow Fe^{2+}$ $Cu + 2Fe^{3+} \rightarrow Cu^{2+} + 2Fe^{2+}$ (reversible arrow-no marks)
	(a)(iv)	$[Fe^{3+}]$ decreases $[Fe^{2+}]$ increases
	(a)(v)	$Cu \rightarrow Cu^{2+} + \mathbf{2e}$ Q = I x t = 30 X 1 = **30 C** Q =nFe 30 x 1 = mass/Mr x 96500 x**2** **mass of Cu dissolves = 9.87 x 10^{-3} g**
	(a)(vi)	Either :The direction of electron flow will be reversed or the direction of current flow will be reversed or voltage increase
	(b)	Equilibrium considerations for mention of shift of POE (Using *Le Chatelier's* principle to predict) suggest the use of a low temperature as the forward exothermic reaction liberates energy for the synthesis of ammonia Whereas a high temperature is favoured for the endothermic reaction in the synthesis of nitrogen monoxide. A catalyst is used to speed up the reaction in the synthesis of ammonia as too high temperature is not favoured
2	**(c)(i)**	Step II : KCN in ethanol, reflux Step III : dilute acid or $H^+(aq)$, boil under reflux
	(c)(ii)	Fe in the presence of excess Cl_2 gives $FeCl_3$ and Cl_2 (not necessary) $FeCl_3 + Cl_2 \rightarrow Cl^+(FeCl_4)^-$ (not necessary) Electrophilic substitution of methyl benzene with Cl^+

		 Intermediate Arrows [1] Intermediate [1]
	(c)(iii)	P = $C_6H_5CH_2COOH$
	(c)(iv)	Step III : acidic hydrolysis Step IV : reduction

3	**(a)**	

Hydrogen Halides	**HC*l***	**HBr**	**HI**
Observations	No observable reactions. White fumes of HC*l* remains.	Reddish brown fumes of bromine observed. OR Reddish brown liquid of bromine observed.	Violet or purple fumes of iodine observed. OR Black deposits of iodine observed.
** [½] for 1-2 correct observations of 3			
Equations	No applicable	See below	See below

<u>HBr</u>

$2HBr(g) + H_2SO_4(l) \rightarrow 2H_2O(l) + SO_2(g) + Br_2(g)$

<u>HI</u>

$2HI(g) + H_2SO_4(l) \rightarrow 2H_2O(l) + SO_2(g) + I_2(g)$

$8HI(g) + H_2SO_4(l) \rightarrow 4I_2(g) + H_2S(g) + 4H_2O(l)$

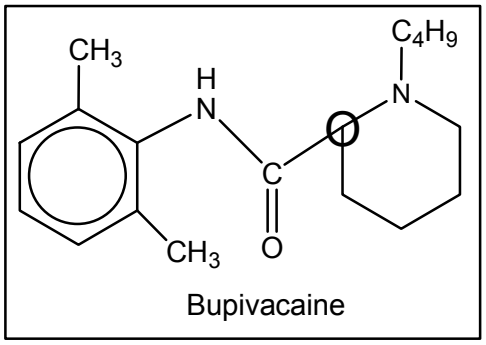
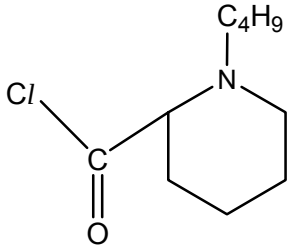
$6HI(g) + H_2SO_4(l) \rightarrow 3I_2(g) + S(s) + 4H_2O(l)$

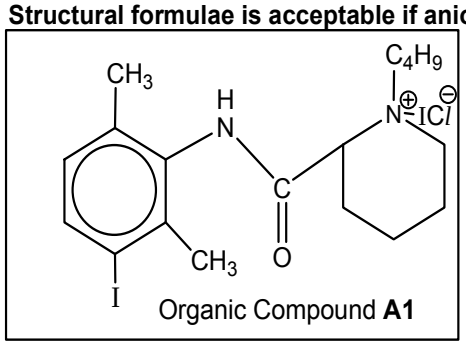
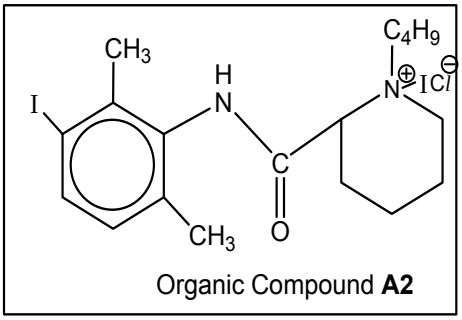
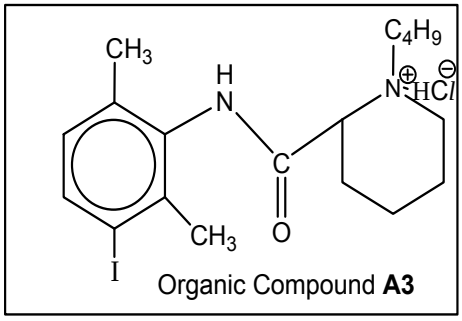
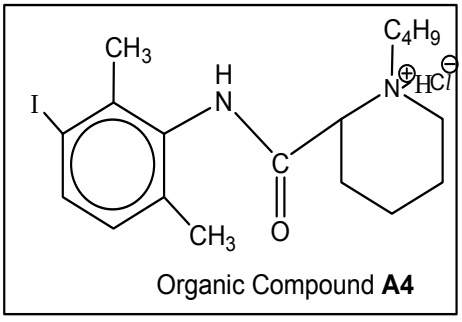
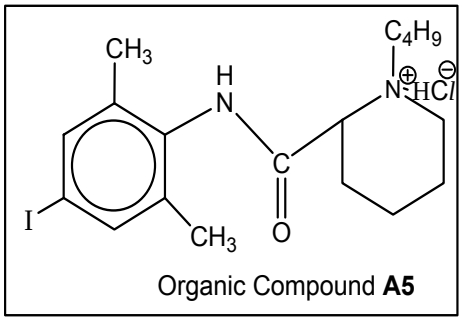
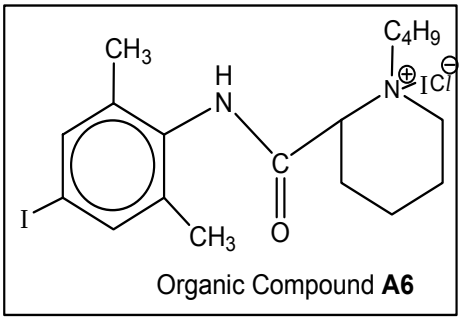
Any 1 equation is acceptable.

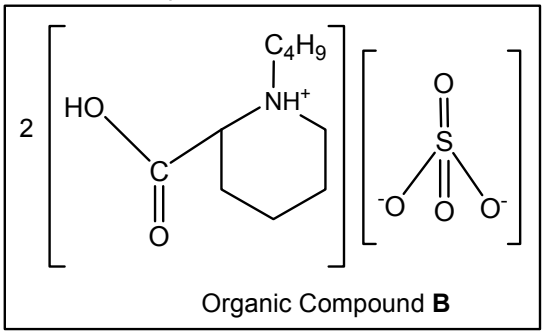
**[1] for 1 correct equations of 2
**[½] for missing state symbols
**[0] for equations that are not balanced

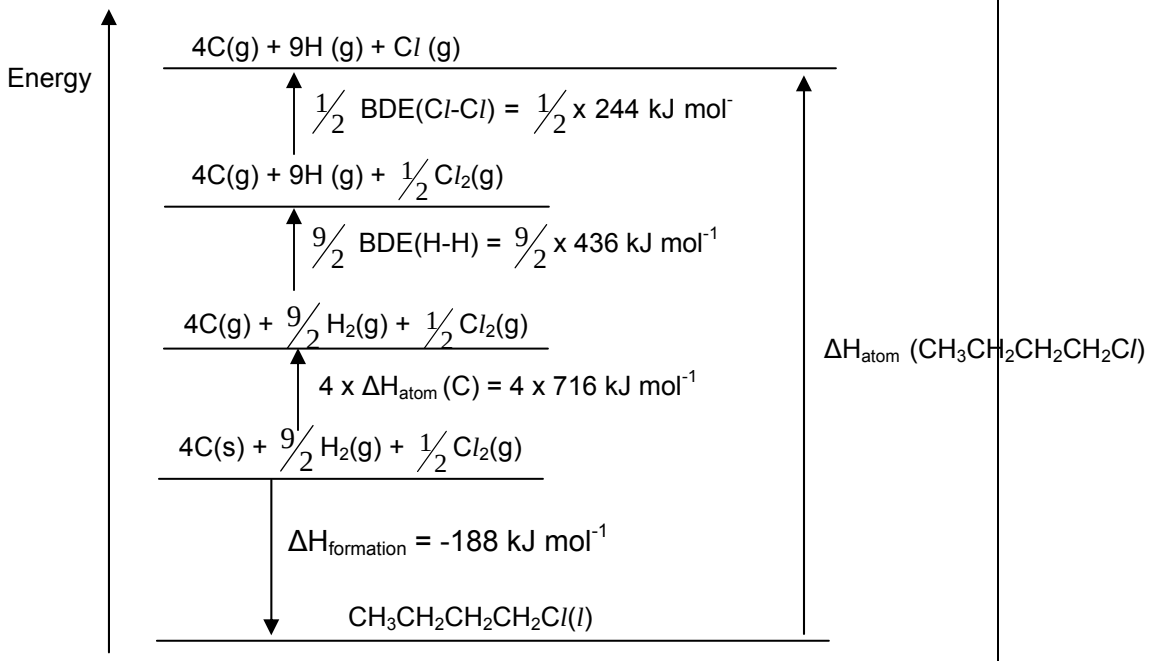
3	**(b)(i) & (ii)**	The breakdown of marks are as follows: • Max of 1m for description • Max of 1m for balanced equation

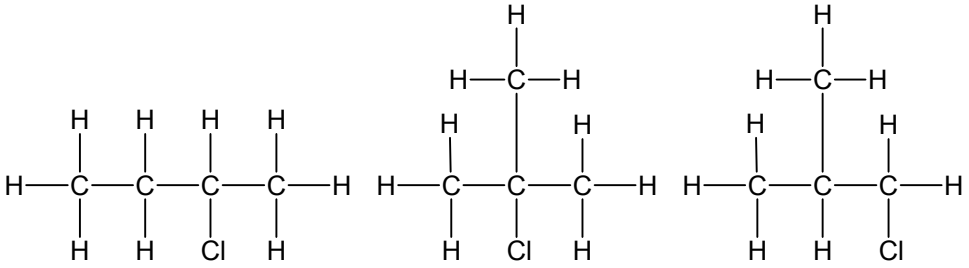
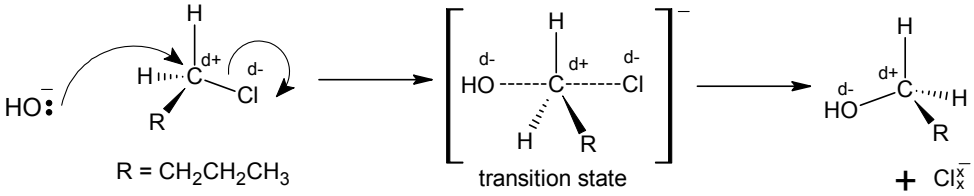
		If state symbols are missing or wrong, [½] for each balanced equation.
3	**(b)(i)**	Cl_2 (g) + $2I^-$ (aq) → $2Cl^-$ (aq) + I_2 (s) I_2 (s) + I^- (aq) ⇌ I_3^- (aq) ---- if not given, it is still acceptable. The iodine that is precipitated gives dark blue colouration with starch solution. If equation is not provided, observations like chlorine displaces iodide are acceptable.
3	**(b)(ii)**	If descriptions are missing, award [2m] for the balanced disproportionation equations. If equations are not provided, award max of 1 m for description like • Disproportionation reactions occur at different temperatures • Disappearance of chlorine smell
	(b)(ii)	With **cold aqueous alkali**, $Cl_2(g) + 2OH^-(aq) \rightarrow Cl^-(aq) + ClO^-(aq) + H_2O(l)$ With **hot aqueous alkali**, $3Cl_2(g) + 6OH^-(aq) \rightarrow 5Cl^-(aq) + ClO_3^-(aq) + 3H_2O(l)$ OR $3ClO^-(aq) \rightarrow 2Cl^-(aq) + ClO_3^-(aq)$
	(c)(i)	**<u>Identification+deductions=Max 3 m</u>** Element **X** : Magnesium Element **Y**: Sulphur Formula of the oxide of Element **Y**: SO_3 6.99g of white ppt correspond to the mass of 0.03 mol of $BaSO_4$ Upon addition of $BaCl_2$, white ppt formed is $BaSO_4$ ▪ $MgCl_2$ **<u>hydrolyses slightly</u>** to form a weakly acidic solution of **<u>pH ~ 6.5</u>** ***<u>Balanced chemical equations MAX: 4 × 1m = 4 m)</u>*** ***<u>[1] for each of any 4 correct equations from equations (i)-(vi)</u>*** $MgO(s) + H_2O(l) \rightarrow Mg(OH)_2(aq)$----------(i) $MgCl_2(s) + 6H_2O \rightarrow [Mg(H_20)_6]^{2+}(aq) + 2Cl^-(aq)$--------(ii) $[Mg(H_2O)_6]^{2+}(aq) \rightleftharpoons [Mg(H_2O)_5(OH)]^+(aq) + H^+(aq)$--------(iii) **OR** $[Mg(H_2O)_6]^{2+}(aq) + H_2O(l) \rightleftharpoons [Mg(H_2O)_5(OH)]^+(aq) + H_3O^+(aq)$-------(iii)

		$SO_3(g) + H_2O(l) \rightarrow H_2SO_4(aq)$-------(iv) $H_2SO_4(aq) + BaCl_2(aq) \rightarrow \underbrace{BaSO_4(s)}_{\text{White ppt}} + 2HCl(aq)$--------(v) $H_2SO_4(aq) + MgO(aq) \rightarrow MgSO_4(s) + H_2O(l)$-------(vi)
3	**(c)(ii)**	Mg (Element **X**) has a **<u>higher melting point</u>** than S_8 (Element **Y**) During melting, **<u>more energy</u>** is required to overcome **<u>the strong metallic bonds</u>** between Mg^{2+} ions and its valence electrons than the **<u>weaker van der waals forces (or id-id interactions)</u>** between S_8 molecules. **If element X and Y are identified wrongly in (c)(i) and candidate gives correct comparison between melting points of a metal and a simple molecule, award 2m accordingly
	(d)(i)	 Bupivacaine 1 chiral carbon atom only.
	(d)(ii)	Reaction **I**: Concentrated HCl, Sn, heat under reflux, then add NaOH(aq)  Reaction **II**: , room temperature

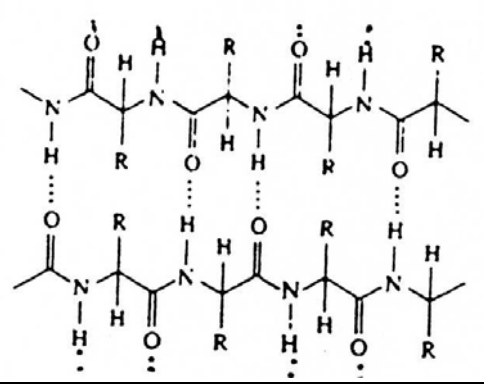
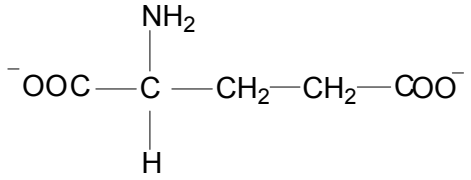
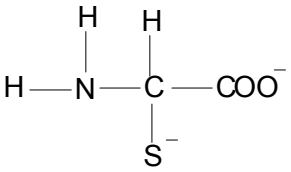
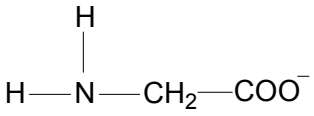
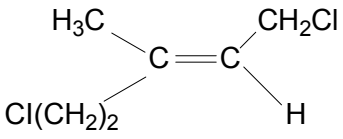
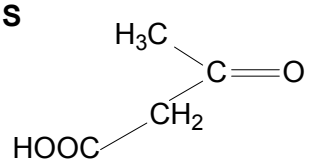
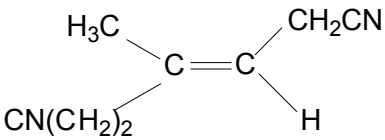
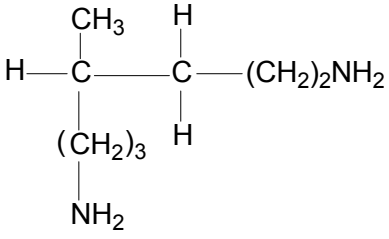
3	**(d)(ii) con't**	**1 mark for any one of the 6 acceptable structural formulae for Organic Compound A** **Structural formulae is acceptable if anion Cl^- is omitted.**  Organic Compound **A1** OR  Organic Compound **A2**  Organic Compound **A3** OR  Organic Compound **A4**  Organic Compound **A5** OR  Organic Compound **A6**

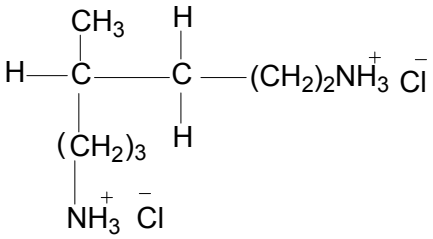
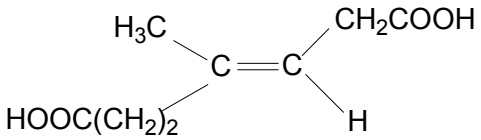
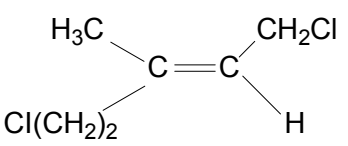
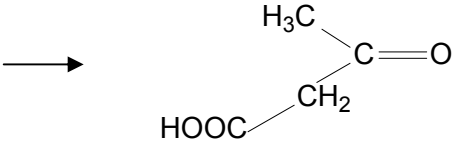
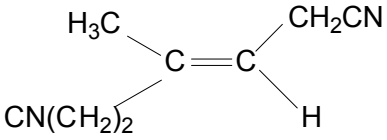
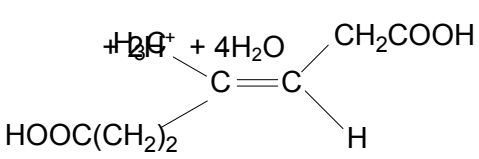
		Structural formula of **B** is acceptable if either SO_4^{2-} or its structural formula is omitted  Organic Compound **B**

4	**(a)(i)**	Enthalpy change of formation is the energy change when **one mole of compound is formed** from its **constituent elements in the standard states at 25°C and 1 atm**.
	(a)(ii)	 Correct diagram with labels (either ΔH or values) Quote BDE of H-H and C*l*-C*l* with correct coefficients (in diagram or working) ΔH_{atom} ($CH_3CH_2CH_2CH_2Cl$) = -(-188) + 4(716) + 9/2 (436) + ½ (244) **= +5140 kJ mol^{-1}**

	(a)(iii)	ΔH_{atom} ($CH_3CH_2CH_2CH_2Cl$) = BDE (C-C*l*) + 3BDE(C-C) + 9BDE(C-H) = 340 + 3(350) + 9(410) = **+5080 kJ mol^{-1}**
	(a)(iv)	Values in Data Booklet are only averages. For (ii), vapourisation of $CH_3CH_2CH_2CH_2Cl(l)$ into gaseous state is not taken into account.
4	**(b)(i)**	
	(b)(ii)	2-chlorobutane, $CH_3CH_2CHClCH_3$ straight-chain isomer with **<u>elongated electron cloud</u>**, **<u>largest surface area</u>** for interaction between molecules Largest amount of energy required to break the **<u>strongest Van der Waals forces</u>** between molecules, hence highest boiling point.
	(c)(i)	NaOH (aq). Reflux.
	(c)(ii)	Nucleophilic substitution.  R = $CH_2CH_2CH_3$ transition state curly arrows transition state
	(c)(iii)	Exothermic. ΔH = Bonds Broken – Bonds Formed = BDE (C-C*l*) – BDE (C-O) = 340 – 360 = **-20 kJ mol^{-1}**
	(c)(iv)	$CH_3CH_2CH_2CH_2OH \longrightarrow CH_3CH_2CH_2CHO$ Dil. H^+ (aq) / $K_2Cr_2O_7$ (aq). Distil. *reflux – [0]; No distil – [0]* $CH_3CH_2CH_2CHO \longrightarrow CH_3CH_2CH_2CH(OH)CN$ HCN with traces of NaOH/ NaCN. 10-20^oC Identify intermediate as $CH_3CH_2CH_2CHO$

5	**(a)(i)**	val-leu-glu-asp-thr-leu-ala-glu-leu-glu-ala
	(a)(ii)	Basically to test whether students remember to subtract **3 H_2O**

		Ans 530-54 = **476**
	(a)(iii)	**β-pleated sheet** 
	(b)(i)	  
	(b)(ii)	electrostatic , disulphide, pd-pd , van der Waals'
5	**(c)(i)** **(c)(i) con't**	• R has a C=C. On vig oxidation, 2C must have been converted to CO_2 • S has a carboxyl fg (reaction with $NaHCO_3$) and a ketone with the group CH_3CO • R to T is a nucleophilic substitution (note same no. of H-atoms) • T is reduced to U, a saturated amine • V is a salt from neutralistion with HCl • T is hydrolysed to a diacid. **R**  **S**  **T**  

		V  **W**  $+ 3OH^- + 4[O]$
	(c)(ii)	 $+H^+$  $+2CO_2 + 2H_2O + 2Cl^-$  $+H_2O$ 

- End of Marking Scheme -