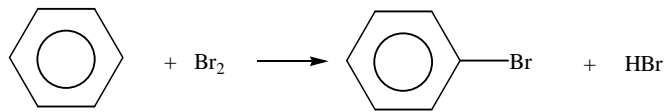
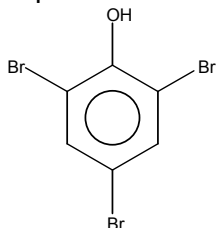
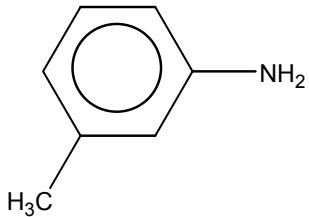
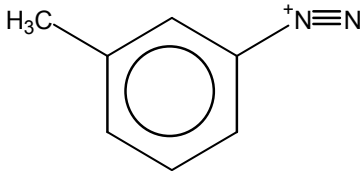
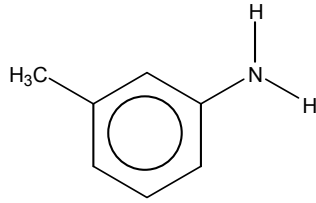
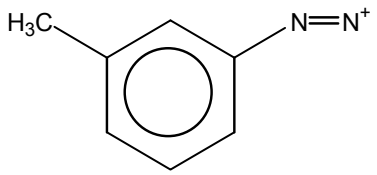
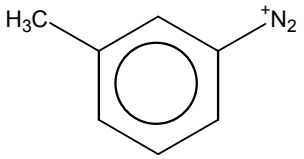
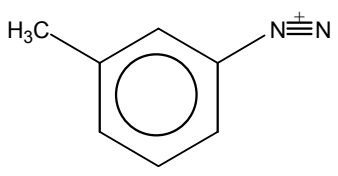
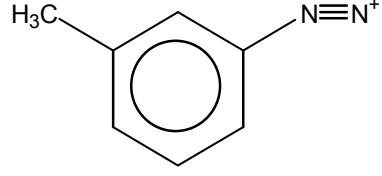
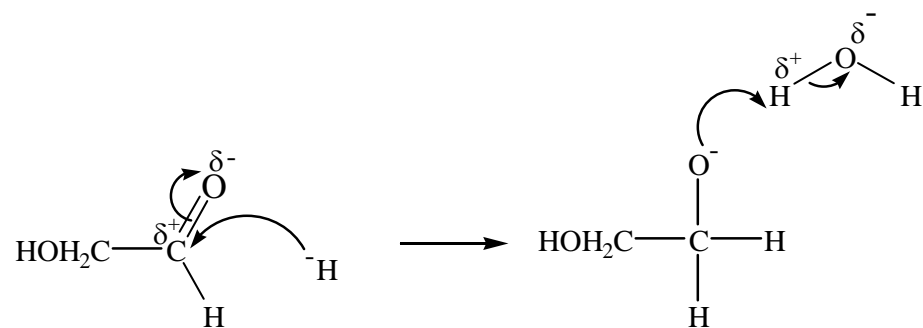
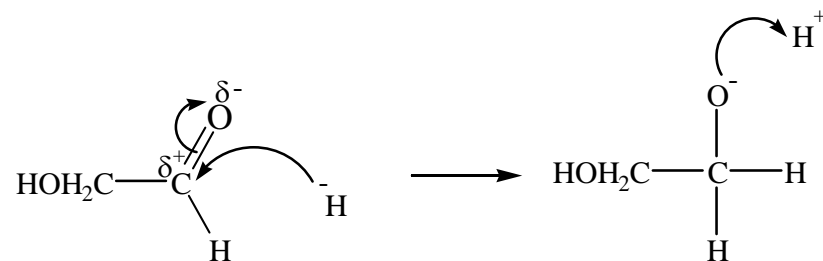


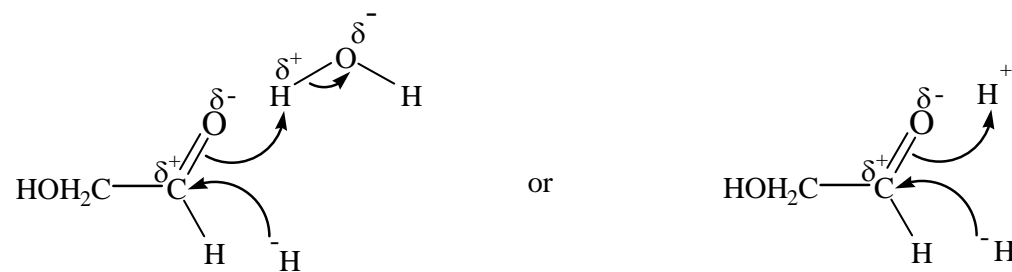
Question			Expected Answers	Marks	Additional Guidance
1	(a)			1	ALLOW $\text{C}_6\text{H}_6 + \text{Br}_2 \longrightarrow \text{C}_6\text{H}_5\text{Br} + \text{HBr}$ DO NOT ALLOW multiple substitution DO NOT ALLOW Br^+
	(b)	(i)	White precipitate OR white solid OR white crystals ✓ 	2	DO NOT ALLOW colourless DO NOT ALLOW white ppt <u>and</u> bubbles DO NOT ALLOW $\text{Br}_3\text{C}_6\text{H}_2\text{OH}$ OR 2,4,6-tribromophenol OR tribromophenol
		(ii)	1,2-Dibromocyclohexane ✓	1	ALLOW 1,2dibromocyclohexane OR 1-2dibromocyclohexane OR 12dibromocyclohexane OR cyclo-1,2-dibromohexane DO NOT ALLOW dibromocyclohexane OR $\text{C}_6\text{H}_{10}\text{Br}_2$ OR structures
		(iii)	MUST spell <u>delocalised/delocalized</u> or <u>localised/localized</u> correctly once in the answer to obtain all 5 marks benzene <u>electrons</u> or <u>π-bonds</u> are delocalised ✓ phenol a <u>lone</u> or <u>non-bonded</u> pair of electrons on the oxygen or the OH group is (partially) delocalised into the ring ✓ cyclohexene electrons are localised OR delocalised between two carbons ✓ benzene has a lower electron density OR phenol has a higher electron density OR cyclohexene has a higher electron density ✓ benzene cannot polarise or induce a dipole in Br_2 OR phenol can polarise the Br_2 OR cyclohexene can polarise Br_2 or the Br–Br bond ✓	5	ALLOW diagram to show overlap of all 6 p-orbitals for delocalisation DO NOT ALLOW benzene has delocalised structure or ring ALLOW diagram to show movement of lone pair into ring for phenol ALLOW diagram or description of overlap of 2 adjacent p-orbitals for bonding in cyclohexene DO NOT ALLOW cyclohexene has a C=C double bond IGNORE slip if cyclohexene is written as cyclohexane but π -bonding correctly described DO NOT ALLOW charge density OR electronegativity instead of electron density ALLOW $\text{Br}^{\delta+}$ OR electrophile Br^+ as alternate to polarise

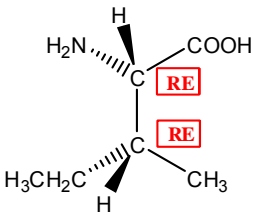
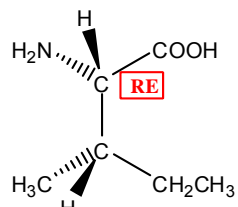
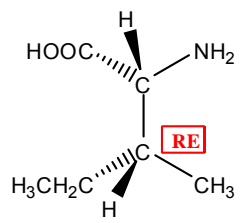
<p>(c)</p>	<div style="text-align: center;">  <p>✓</p> </div> <div style="text-align: center;">  <p>✓✓</p> </div> <div style="border: 1px solid black; padding: 5px; margin: 10px auto; width: fit-content;"> ALLOW ECF ✓✓ on incorrect amine </div> <p>HNO₂ + HCl and temp < 10 °C OR NaNO₂ + HCl and temp < 10 °C ✓</p> <p>alkaline AND phenol (if temperature stated must be below 10 °C) ✓</p>	<p>Total 14</p>	<p>ALLOW</p> <div style="text-align: center;">  </div> <p>IGNORE Cl⁻ ion</p> <p>DO NOT ALLOW if ring is connected to the N triple bond in the diazonium or if diazonium has a negative charge</p> <p>ALLOW one mark for correct displayed diazonium if alkyl group is not shown</p> <div style="display: flex; justify-content: space-around;"> <div style="text-align: center;"> <p>ALLOW</p>  <p>for both marks</p> </div> <div style="text-align: center;"> <p>ALLOW</p>  <p>for one mark</p> </div> </div> <div style="display: flex; justify-content: space-around;"> <div style="text-align: center;"> <p>ALLOW</p>  <p>for one mark</p> </div> <div style="text-align: center;"> <p>ALLOW</p>  <p>for one mark</p> </div> </div> <p>ALLOW NaOH OR KOH & C₆H₅OH OR phenoxide ion OR C₆H₅O⁻</p> <p>ALLOW reagents and conditions from the equations</p>
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Question			Expected Answers	Marks	Additional Guidance
2	(a)	(i)	<u>silver</u> mirror ✓	1	ALLOW Ag(s) OR Ag mirror OR precipitate OR ppt OR solid ALLOW brown OR black OR grey
		(ii)	HOCH ₂ COOH ✓	1	ALLOW CH ₂ OHCOOH OR CH ₂ OHCO ₂ H OR HOCH ₂ CO ₂ H OR displayed OR skeletal formula OR HOCH ₂ COO ⁻ DO NOT ALLOW C ₂ H ₄ O OR 2-hydroxyethanoic acid
	(b)		$\text{HOCH}_2\text{CHO} + 3[\text{O}] \rightarrow \text{HOCCOOH} + \text{H}_2\text{O}$ <div style="display: flex; justify-content: space-around; width: 100%;"> reagents ✓ both products ✓ </div>	2	ALLOW displayed/skeletal formula/COOHCOOH ✓✓ if molecular formula used C ₂ H ₄ O ₂ + 3[O] → C ₂ H ₂ O ₄ + H ₂ O max = 1 ✓ Any correctly balanced equation for partial oxidation can score 1 mark ✓ HOCH ₂ CHO + [O] → HOCH ₂ COOH OR HOCH ₂ CHO + 2[O] → OHCCOOH + H ₂ O OR HOCH ₂ CHO + [O] → OHCCHO + H ₂ O OR HOCH ₂ CHO + 2[O] → HOOCCHO + H ₂ O
	(c)	(i)	HOCH ₂ CH ₂ OH ✓	1	ALLOW HO(CH ₂) ₂ OH OR (CH ₂ OH) ₂ OR skeletal formula OR displayed formula DO NOT ALLOW molecular formula (C ₂ H ₆ O ₂)
		(ii)	curly arrow from H ⁻ to C ^{δ+} ✓ dipoles <u>and</u> curly arrow from C=O bond to O ✓ intermediate ✓ curly arrow from intermediate to H ^{δ+} in H ₂ O/ H ⁺ and if H ₂ O is used it must show the curly arrow from the O–H bond to the O ✓ <i>lone pairs are not essential</i>	4	ALLOW curly arrow to C even if dipole missing or incorrect ALLOW maximum of 3 marks if incorrect starting material is used See page 36 for detailed mechanisms – Alternative 3 scores all 4 marks even though the intermediate is not shown

Alternative 1**Alternative 2**

products
are not
required

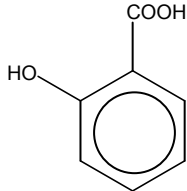
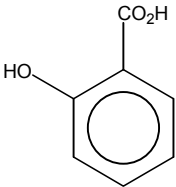
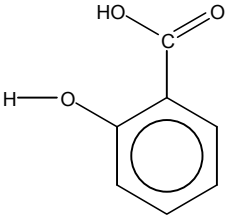
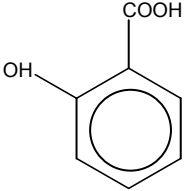
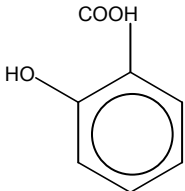
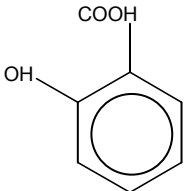
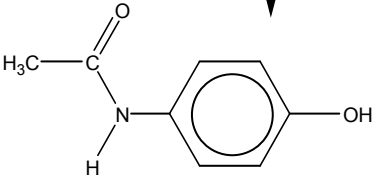
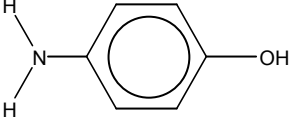
Alternative 3**Total****9**

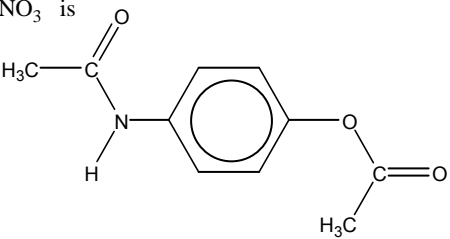
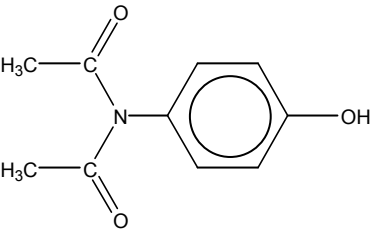
Question			Expected Answers	Marks	Additional Guidance
3	(a)	(i)	adsorption ✓	1	ALLOW partition OR adsorbition IGNORE solubility OR desorption DO NOT ALLOW absorption
		(ii)	measure how far each spot travels relative to the solvent front or calculate the R_f value ✓ compare R_f values to those for known amino acids ✓	2	ALLOW compare R_f values to database ALLOW compare to known amino acids DO NOT ALLOW retention times for first mark, but the 2nd mark would be available as ✓ ECF ALLOW alternative approach: on the same plate compare position of spots ✓ with known amino acids ✓
		(iii)	(amino acids won't separate because) similar compounds have similar R_f (values) ✓	1	ALLOW spots often overlap OR don't (fully) separate ALLOW they have similar R_f (values) or similar adsorptions or similar retention times ECF to a(ii)
	(b)	(i)	$\begin{array}{c} \text{H} \\ \\ \text{H}_2\text{N}-\text{C}-\text{COOH} \\ \\ \text{R} \end{array}$ ✓	1	ALLOW $\text{RCH}(\text{NH}_2)\text{COOH}$ any order for R, NH_2 and COOH but C must be next to H ' <u>CH</u> ' must be shown ALLOW CO_2H brackets around NH_2 are not essential ALLOW structure
		(ii)	must attempt 3D use RE symbol in the "tools" to denote whether or not each chiral C is a reflection of the one given in the question <div style="display: flex; justify-content: space-around; align-items: flex-start;"> <div style="text-align: center;">  <p>both chiral Cs are mirror images</p> </div> <div style="text-align: center;">  <p>top chiral C only is a mirror image</p> </div> <div style="text-align: center;">  <p>bottom chiral C only is a mirror image</p> </div> </div>	3	each chiral C must have 2 — bonds, 1 wedge bond (IGNORE shading) & 1 dash bond (IGNORE wedge) check the clockwise orientation of each C. For each C start with the H and if on the: <ul style="list-style-type: none"> top C the H is followed by COOH it is not a mirror image. If it is a mirror image annotate using RE. bottom C the H is followed by CH_3 it is not a mirror image. If it is a mirror image annotate using RE. the four groups can be attached in any order. If the molecule is drawn upside down – clockwise becomes anti-clockwise. MUST check that the drawn structure is non-superimposable irrespective of the orientation or the way it has been drawn. IGNORE bond linkage for all groups

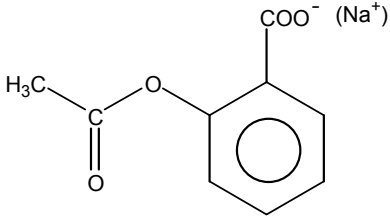
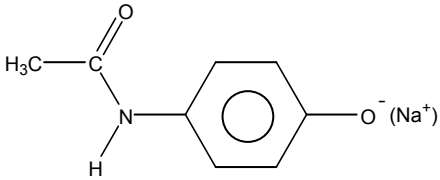
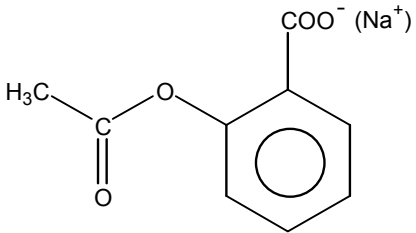
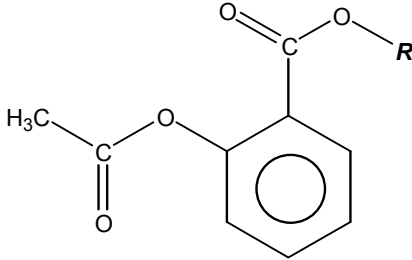
	(c)	<div style="display: flex; justify-content: space-around; align-items: center;"> <div style="text-align: center;"> $\begin{array}{c} \text{H} \\ \\ \text{H}_3\text{N}^+ - \text{C} - \text{COO}^- \\ \\ \text{CH}_3 \end{array}$ <p>alanine at pH = 6.0 ✓</p> </div> <div style="text-align: center;"> $\begin{array}{c} \text{H} \\ \\ \text{H}_2\text{N} - \text{C} - \text{COO}^- \\ \\ (\text{CH}_2)_2 \\ \\ \text{COO}^- \end{array}$ <p>glutamic acid at pH = 10 ✓</p> </div> <div style="text-align: center;"> $\begin{array}{c} \text{H} \\ \\ \text{H}_3\text{N}^+ - \text{C} - \text{COOH} \\ \\ (\text{CH}_2)_4 \\ \\ ^+\text{NH}_3 \end{array}$ <p>lysine at pH = 2.0 ✓</p> </div> </div>		<p>ALLOW CO_2^-</p> <p>ALLOW NH_3^+</p> <p>If NH_3 fully displayed ALLOW + charge on N or H</p> <p>If COO fully displayed ALLOW $-$ charge on O only</p>
	(d)	valine–glycine–leucine ✓	1	<p>ALLOW val–gly–leu</p> <p>DO NOT ALLOW structures</p>
	(e)	$\text{H}_2\text{N}(\text{CH}_2)_6\text{NH}_2$ ✓ $\text{HOOC}(\text{CH}_2)_8\text{COOH}$ ✓	2	<p>ALLOW $\text{H}_2\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$</p> <p>ALLOW $\text{HOOCCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{COOH}$</p> <p>ALLOW CO_2H for COOH</p> <p>ALLOW acid chloride, $\text{ClOC}(\text{CH}_2)_8\text{COCl}$</p> <p>ALLOW displayed formulae or skeletal formulae</p>
		Total	14	

Question		Expected Answers	Marks	Additional Guidance
4	(a)	<p>infrared – 1 mark only shows (very broad) peak between 2500–3300 (cm^{-1}) (due to O–H bond) ✓</p> <p>^{13}C NMR – 2 marks (CH_3)₂CHCH₂COOH has 4 peaks (due to 4 different C environments) ✓ (CH_3)₃CCOOH has 3 peaks (due to 3 different C environments) ✓</p>	3	<p>ALLOW (very broad) peak around 3000 (cm^{-1}) OR any stated value between 2500 and 3300 (cm^{-1}) for O–H DO NOT ALLOW peak in range 3200–3550 (cm^{-1})</p> <p>IGNORE any reference to C=O or C–O as both are also present in an ester OR to fingerprint region</p> <p>ALLOW '^{13}C NMR detects the number of/different C environments' for 1 ✓, suitable example for the 2nd mark</p>
	(b)	<p>splitting pattern explains any two in terms of '$n + 1$ rule' for two marks ✓✓ Explains any one peak for 1 mark ✓</p> <ul style="list-style-type: none"> • <i>singlet</i> therefore adjacent C (if any) has no Hs • <i>multiplet</i> OR split into 7 therefore adjacent Cs have lots of/6 Hs • <i>doublet</i> therefore adjacent C is bonded to 1H <p>must spell one of <i>multiplet / heptet, singlet, doublet</i> correctly</p> <p style="text-align: right;">max = 2 marks</p> <p>chemical shifts</p>	6	<p>1 mark for correct ester</p> <p>if two splitting patterns are correctly analysed ignore the third</p> <p>ALLOW singlet because next or bonded to an O</p> <p>ALLOW multiplet/heptet because next to 2 CH_3s</p> <p>ALLOW doublet because next to a CH</p> <p>ALLOW tolerance on δ values; 3.6–3.8, 2.6–2.8 and 1.1–1.3</p>

		<p>two marks if any two absorptions are identified correctly ✓✓ one mark if any one absorption is identified correctly ✓</p> <ul style="list-style-type: none"> • peak ~3.7 (ppm) – bonded to an O • peak ~2.7 (ppm) – indicates it is next to a C=O • peak ~1.2 (ppm) – bonded to other Cs OR part of a chain <p style="text-align: right;">max = 2 marks</p> <p>compound identified as $(\text{CH}_3)_2\text{CHCOOCH}_3$ ✓✓ 2 marks</p> <p>compound identified as $\text{CH}_3\text{COOCH}(\text{CH}_3)_2$ ✓ 1 mark</p>		<p>(ppm)</p> <p>ALLOW any two gets 2 marks, any one scores 1 mark</p> <div style="display: flex; justify-content: space-around; align-items: flex-end;"> <div style="text-align: center;"> $\text{HC}—\text{O}$ 3.7 (ppm) </div> <div style="text-align: center;"> $\text{HC}—\text{C} \begin{array}{l} \nearrow \text{O} \\ \searrow \end{array}$ 2.7 (ppm) </div> <div style="text-align: center;"> $\text{R}—\text{CH}$ 1.2 (ppm) </div> </div> <p>ALLOW peaks labelled on the spectrum ALLOW singlet must be bonded to O, multiplet to C=O and doublet to CH or R for both chemical shift marks</p> <p>if two chemical shifts are correctly identified IGNORE the third</p>
		Total	9	

Question	Expected Answers	Marks	Additional Guidance
5 (a)	 ✓	1	<p>ALLOW</p>  or  DO NOT ALLOW incorrect bond linkage  or  or 
(b) (i)	<p>equation</p> $(\text{CH}_3\text{CO})_2\text{O} + \text{H}_2\text{N}-\text{C}_6\text{H}_4-\text{OH}$ <p style="text-align: right;">reactants ✓</p> <p style="text-align: center;">↓</p> <div style="display: flex; align-items: center; justify-content: center;"> <div style="text-align: center;">  </div> <div style="margin: 0 10px;">+ CH₃COOH</div> <div style="text-align: center;"> <p>products ✓</p> </div> </div>	2	<p>ALLOW</p> $(\text{CH}_3\text{CO})_2\text{O} + \text{H}_2\text{NC}_6\text{H}_4\text{OH} \rightarrow \text{CH}_3\text{CONHC}_6\text{H}_4\text{OH} + \text{CH}_3\text{COOH}$ <p>ALLOW</p>  DO NOT ALLOW molecular formulae

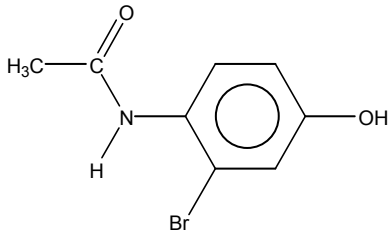
		(ii)	<p>$C_{10}H_{11}NO_3$ is</p>  <p>or</p>  <p style="text-align: right;">✓</p>	1	<p>ALLOW amide shown as either CH_3CONH- OR $H_3CCONH-$ OR CH_3COHN- OR $H_3CCOHN-$</p> <p>ALLOW ester shown as either $-OCOCH_3$ OR $-OOCCH_3$</p>
		(iii)	<p>to ensure that there are no (harmful) side effects ✓</p>	1	<p>ALLOW impurities reduce effectiveness (of drug) OR might be toxic OR avoids litigation OR harmful OR hazardous</p> <p>ALLOW to ensure that the drug/active component is safe</p> <p>IGNORE dangerous OR nasty OR can kill OR increased dosage</p>
	(c)		<p>(aspirin contains) ester AND carboxylic acid ✓</p> <p>(paracetamol contains) amide AND phenol ✓</p>	2	<p>IGNORE arene or benzene or aromatic or phenyl or methyl but any other group loses the mark</p> <p>ALLOW carboxyl group</p> <p>DO NOT ALLOW acid</p> <p>IGNORE arene or benzene or aromatic or phenyl or methyl but any other group loses the mark</p> <p>ALLOW peptide</p> <p>ALLOW hydroxy(l)</p> <p>DO NOT ALLOW hydroxide or alcohol</p> <p>DO NOT ALLOW amine</p>
	(d)	(i)	Both	3	ALLOW hydrolysis by $H^+(aq)$ or H^+ or $HCl(aq)$ or HCl or $H_2SO_4(aq)$

		<p>Na OR NaOH ✓</p>  <p>from aspirin</p>  <p>from paracetamol</p> <p>✓</p> <p>✓</p>	<p>or H₂SO₄ to give hydroxybenzoic acid + ethanoic acid with aspirin ✓ and ammonium salt of 4-aminophenol + ethanoic acid with paracetamol ✓</p> <p>ALLOW hydrolysis by OH⁻(aq) or NaOH(aq) and other alkali leading to hydrolysis to give carboxylate salt and phenoxide salt on the ring + ethanoate with aspirin ✓ and 4-aminophenoxide ion + ethanoate ion with paracetamol ✓</p> <p>ALLOW HNO₃ (and H₂SO₄) to give NO₂ in one or more positions on the ring in both aspirin and paracetamol ✓✓</p> <p>DO NOT ALLOW NH₃ but correct ammonium salts can be awarded 2 marks ECF</p> <p>DO NOT ALLOW H₂O but correct products can be awarded 2 marks ECF</p> <p>if no reagent there cannot be any marks for the products If reagent selected is incorrect but would react with either aspirin or paracetamol ALLOW ✓ ECF for the correct organic product</p>
	(ii)	<p>aspirin only NaHCO₃ OR Na₂CO₃ OR metal oxide ✓</p>  <p>✓</p>	<p>2</p> <p>ALLOW Mg, carbonates, NH₃ ALLOW alcohols (ROH) to give ester if no reagent there cannot be any marks for the products</p>  <p>If reagent selected is incorrect but would react with BOTH aspirin and paracetamol ALLOW ✓ ECF for the correct organic product</p>
	(iii)	<p>paracetamol only</p>	<p>ALLOW Br₂ water</p>

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Mark Scheme

January 2010

			<p>Br₂ ✓</p>  <p style="text-align: right;">✓</p>	<p>2</p>	<p>ALLOW one or more Br at any position on the ring DO NOT ALLOW Br substitution of OH ALLOW acyl chloride or acid anhydride and corresponding ester ALLOW FeCl₃ to form a purple <u>complex ion</u> (structure not required) ALLOW diazonium and structure showing azo group substituting one of the Hs in the ring if no reagent there cannot be any marks for the products</p> <p>If reagent selected is incorrect but would react with BOTH aspirin and paracetamol ALLOW ✓ ECF for the correct organic product</p>
			Total	14	

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