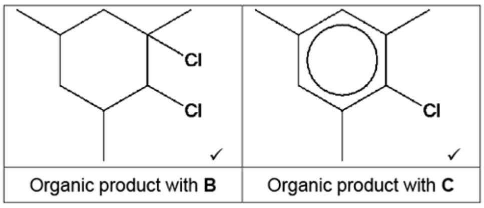
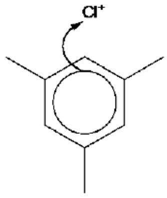
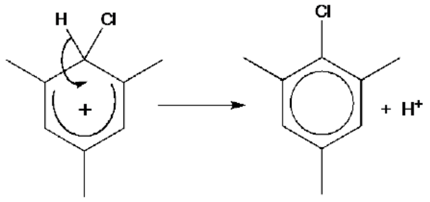
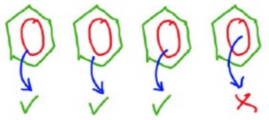
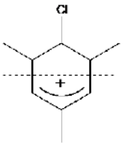
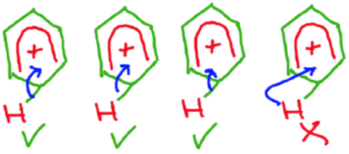
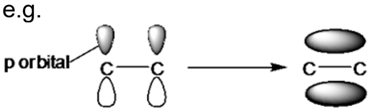
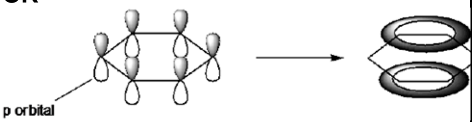
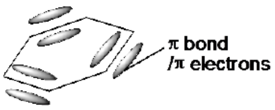
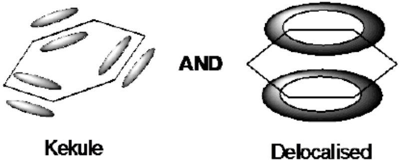
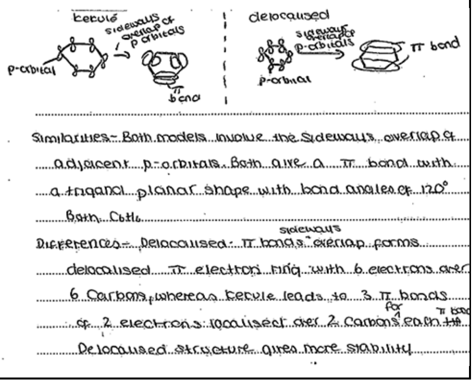
Mark scheme – Aromatic Compounds

Question			Answer/Indicative content	Marks	Guidance
1		i	 Organic product with **B** · Organic product with **C**	2 (AO2.5 ×2)	
		ii	**Reactivity of B** in B electrons are localised OR in B π-bond is localised ✓ **Reactivity of C** in C electrons are delocalised OR In C π-system / ring is delocalised In **B**, electron density is higher **AND** B is more susceptible to electrophilic attack **OR** B attracts/accepts the electrophile/Cl_2 more **OR** B polarises the electrophile/Cl_2 more ✓ **ORA**	3 (AO1.1 ×3)	**ALLOW** labelled diagram to show delocalised system **IGNORE** charge density **IGNORE** electronegativity **IGNORE** B is more reactive/reacts more readily (no reference to electrophile) **IGNORE** references to electron density spread around the π−ring ALLOW chlorine **<u>Examiner's Comments</u>** Candidates answered this question well. Many were able to correctly use the terms delocalised and localised in their responses and were able to provide comparisons for both electron density and attack of an electrophile.
		iii	**Generation of electrophile** $AlCl_3 + Cl_2 \rightarrow AlCl_4^- + Cl^+$ ✓ Attack of Cl^+  Curly arrow from π-bond to Cl^+ ✓ -- **Intermediate and organic product**	5 (AO1.2) (AO1.2) (AO2.5) (AO1.2) (AO1.2)	ANNOTATE ANSWER WITH TICKS AND CROSSES **ALLOW** $FeCl_3 + Cl_2 \rightarrow FeCl_4^- + Cl^+$ **ALLOW** use of Fe **NOTE**: curly arrows can be straight, snake-like, etc. .... but **NOT** double-headed or half-headed arrows **1st curly arrow** must • start from, **OR** close to, **circle of benzene ring**

			 Correct intermediate ✓ Curly arrow from C–H bond to reform π-ring ✓ -- **Regeneration of catalyst** $H^+ + AlCl_4^- \rightarrow AlCl_3 + HCl$ ✓		 **DO NOT ALLOW** following intermediate:  π-ring must cover 4 of the 6 sides of the benzene ring **AND** correct orientation, *i.e.* gap towards C–Cl **ALLOW** + sign anywhere inside the ‘hexagon’ of the intermediate. **IGNORE** partial charges on the chlorine in the intermediate **DO NOT ALLOW** mark for intermediate if any CH_3 is missing **Curly arrow** must start from, **OR** be traced back to, **any part of** C-H bond and go inside the ‘hexagon’  **ALLOW** use of $AlCl_4^-$ in the mechanism **ALLOW** ECF for regeneration of an incorrect metal chloride catalyst e.g. $AgCl_3$
			Total	**10**	
2		i	**Similarities** **Orbital overlap** (sideways) overlap of **p** orbitals ✓ **π bond** π bond/system/ring above and below (bonding (C) atoms/ring/plane) ✓ **Difference** Kekule has: alternating π bonds OR 3 π bonds / localised (π electrons) / overlap in one direction / 2 electrons in π bond **AND**	3(AO 1.1 × 3)	**ANNOTATE ANSWER WITH TICKS AND CROSSES ETC** **ALLOW** diagram showing orbital overlap e.g.  **OR**  p orbital label is **required** for first mark **IGNORE** C=C in diagram showing π bond **IGNORE** reference to s orbital overlap/σ bonds

			Delocalised has: π ring (system) / all p orbitals overlap OR (π electrons) spread around ring / overlap in both directions / 6 electrons in π bond /		--- **ALLOW** from labelled diagram showing π bond e.g.  OR  π bond/π electrons label is **required** for second mark --- **ALLOW** diagram showing π bond in **both** Kekule **AND** delocalised models e.g  π bond labels **not** required for third mark **<u>Examiner's Comments</u>** Candidates found this question difficult. The majority of the cohort referred to the overlap of p orbitals in either the Kekulé or delocalised model. The best responses developed this idea further and made reference to π bonds above and below the bonding carbon atoms. Although some candidates were able describe the difference between the two models, the responses of others lacked detail. Describing conceptual ideas, such as orbital overlap and π bonds, is understandably tricky. Candidates are advised to draw diagrams. These serve as a good basis from which to construct a written response. Exemplar 5 shows how effective the use of diagrams can be. **Exemplar 4**  Similarities:- Both models involve the sideways overlap of adjacent p-orbitals. Both are a π bond with a trigonal planar shape with bond angles of 120° Both C_6H_6 Differences:- Delocalised: π bonds sideways overlap forms delocalised π electron ring with 6 electrons over 6 carbons, whereas kekule leads to 3 π bonds of 2 electrons localised over 2 carbons for each π bond. Delocalised structure gives more stability

					This response starts with a diagram for both the Kekulé and delocalised models of benzene. Each diagram is clear and shows the p orbitals and π bonds separately. This is an excellent response for future candidates to follow. The candidate's written response is effectively a description of the diagrams they have drawn and describes the similarities and differences between these two models clearly. This response scored full marks and demonstrates the best style of response seen in this part.
		ii	**Any 2 pieces of evidence from (✓ ✓)** **Bond length** (C–C) bond length is between single (C–C) and double bond (C=C) **OR** all (C–C) bond lengths are the same ***ΔH* hydrogenation** *ΔH* hydrogenation less (exothermic) than expected **Resistance to reaction** Benzene is less reactive than alkenes **OR** bromination of benzene requires a catalyst/halogen carrier **OR** benzene does not react with/decolourise bromine (at room temperature) **OR** benzene reacts by substitution **OR** benzene does not (readily) react by addition	2(AO 1.1 ×2)	**ALLOW** (C–C) bond enthalpy is between single (C–C) and double bond (C=C) **OR** all (C–C) bond enthalpies are the same **IGNORE** enthalpy of hydration Benzene is unreactive is **not** sufficient *(no comparison to alkene)* For halogen carrier, **ALLOW** name or formula of suitable catalyst e.g. Fe, $AlCl_3$, $FeBr_3$ **Examiner's Comments** Candidates were well prepared for this question and the majority of the cohort scored two marks. The most common piece of evidence given was the lack of reactivity of benzene with bromine, with candidates citing the need for a catalyst for the reaction to occur. Responses also included reference to carbon-carbon bond lengths as well as the enthalpy of hydrogenation. A small but significant proportion of the cohort referred to hydration rather than hydrogenation.
			Total	**5**	
3			*Refer to marking instructions on page 5 of mark scheme for guidance on marking this question.* **Level 3 (5–6 marks)** Describes, in detail, electrophilic reactions and mechanisms of one aliphatic **AND** one aromatic compound. *There is a well-developed line of reasoning which is clear and logically structured. The information presented is relevant and substantiated.*	6	**Indicative scientific points may include:** **Explanation of role of electrophiles in organic chemistry** **Reaction of aliphatic compound and mechanism**

Level 2 (3–4 marks)

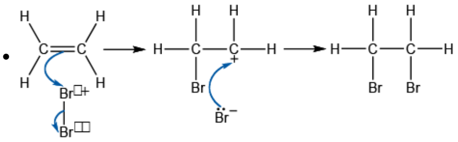
Describes, in detail, an electrophilic reaction and mechanism of one aliphatic **OR** one aromatic compound.
OR
Describes electrophilic reactions and mechanisms of one aliphatic **AND** one aromatic compound, with few omissions/errors.

There is a line of reasoning presented with some structure. The information presented is relevant and supported by some evidence.

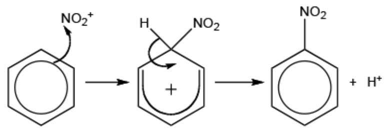
Level 1 (1–2 marks)
Selects suitable reagents for electrophilic reactions of one aliphatic **AND** one aromatic compound.
OR
Attempts to describe an electrophilic reaction and mechanism of one aliphatic **OR** one aromatic compound, with omissions/errors.

There is an attempt at a logical structure with a line of reasoning. The information is in the most part relevant.

0 marks No response or no response worthy of credit.

- Suitable reaction, e.g. ethene and Br_2
  May be shown within mechanism
  Mechanism, e.g.
- 

Reaction of aromatic compound and mechanism

- Suitable reaction, e.g. benzene + Cl_2 ; HNO_3
  May be shown within mechanism
  Mechanism, e.g.
- 

Examples of a detailed description (NOT INCLUSIVE)

- Electrophile as electron pair acceptor
- Types and names of mechanisms
- Equations for generation of electrophile and regeneration of catalyst
- Accurately positioned and directed curly arrows and charges/ dipoles included
- Explanation of major and minor product from electrophilic addition

Examiner's Comments

Overall, this part was answered well.

Good answers were well organised, showing clear mechanisms with precisely positioned curly arrows.

Most candidates included a clear definition of an electrophile and were able to select appropriate reactions. Most candidates were familiar with the mechanisms for electrophilic addition and electrophilic substitution. Mechanisms of an alkene with HBr or Br2 and benzene with NO_2^+ or Br^+ were the most commonly seen. Most candidates showed the role of a catalyst in electrophilic substitution.

Common errors/omissions were the direction of the curly arrow from the aromatic ring to the electrophile, the position of the curly arrow when H^+ is lost from an aromatic intermediate, and not showing the lone pair when Br^- attacks a carbocation.

Some answers lacked detail and gave only two mechanisms with minimal supporting words.

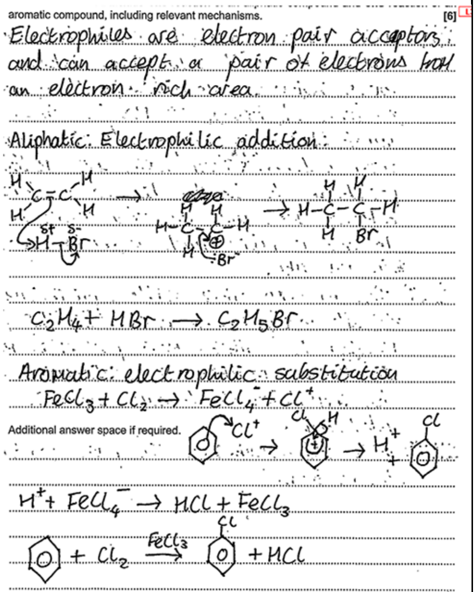
Lower ability candidates described nucleophilic addition or substitution as one of their mechanisms or had curly arrows going in the wrong direction.

A few candidates answered in prose without including equations or diagrams. Candidates are advised that mechanisms must always be communicated in the usual diagrammatic way.

Exemplar 16 is a very clear and concise response showing all the key features of electrophilic addition and electrophilic substitution, including the role of the $FeCl_3$ catalyst. Curly arrows are precisely positioned, with correct use of lone pairs and charges. The candidate has demonstrated excellent knowledge and understanding.

The response in Exemplar 17 is clearly at a different level. The candidate has chosen an alkane rather than an alkene and has used curly arrows and charges incorrectly. This candidate appears to have been poorly prepared.

Exemplar 16



aromatic compound, including relevant mechanisms. [6]

Electrophiles are electron pair acceptors and can accept a pair of electrons from an electron rich area

Aliphatic: Electrophilic addition:

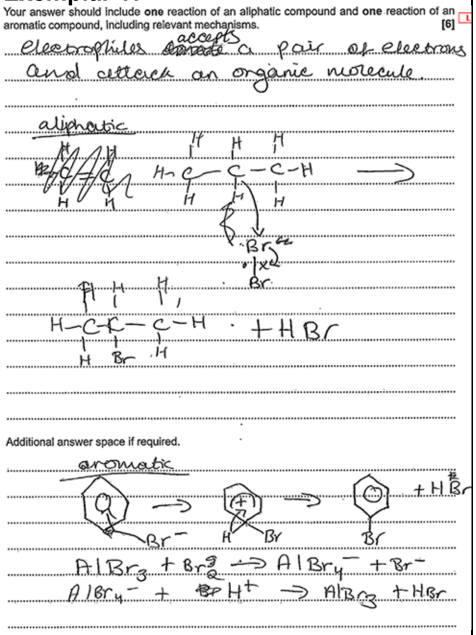
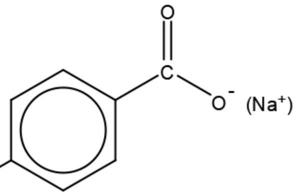
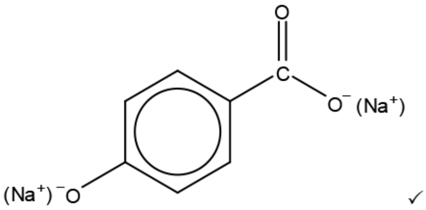
$C_2H_4 + HBr \longrightarrow C_2H_5Br$

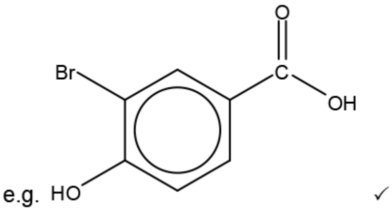
Aromatic: electrophilic substitution

$FeCl_3 + Cl_2 \rightarrow FeCl_4^- + Cl^+$

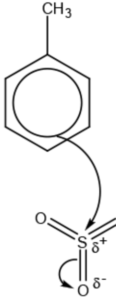
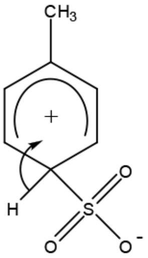
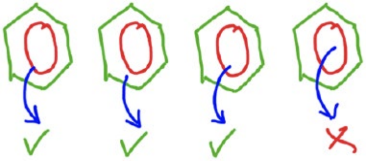
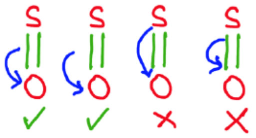
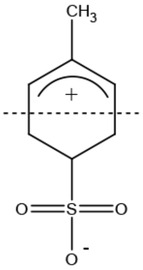
Additional answer space if required.

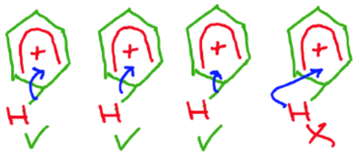
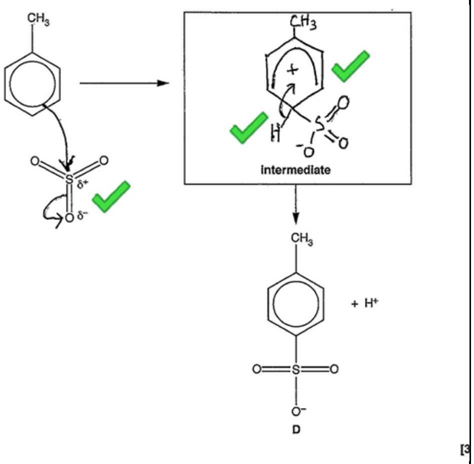
$H^+ + FeCl_4^- \rightarrow HCl + FeCl_3$

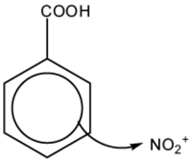
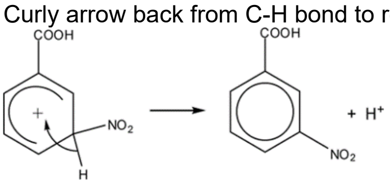
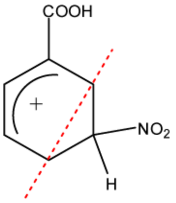
					Exemplar 17  Your answer should include **one** reaction of an aliphatic compound and **one** reaction of an aromatic compound, including relevant mechanisms. **[6]** electrophiles ~~donate~~ accepts a pair of electrons and attack an organic molecule. aliphatic + HBr Additional answer space if required. aromatic + HBr $AlBr_3 + Br_2 \rightarrow AlBr_4^- + Br^-$ $AlBr_4^- + H^+ \rightarrow AlBr_3 + HBr$
			Total	**6**	
4			**Product from Na_2CO_3**  ✓ -- **Product from NaOH(aq)**  ✓ --	**3**	**ALLOW** any combination of skeletal **OR** structural **OR** displayed formula as long as unambiguous **ALLOW** $–COO^-$ **OR** –COONa **DO NOT ALLOW** negative charge on C atom **DO NOT ALLOW** –COO–Na (covalent bond) **IGNORE** connectivity of phenol OH group *(marks are for correct conversions)* **ALLOW** 1 mark if top two structures are shown in wrong boxes

			Product from Br_2  e.g. ✓		**ALLOW** substitution of any H from benzene ring **ALLOW** multiple substitution, *i.e.* di-, tri- and tetrabromo products. **IGNORE** connectivity of phenol OH group *(marks are for correct conversions)* **<u>Examiner's Comments</u>** This question assessed different reactions of compound **H**, 4-hydroxybenzoic acid, and discriminated well. Two of the reactions focused on acid-base chemistry, using the reagents Na_2CO_3 and NaOH. Many candidates recognised that the carboxylic acid group would react in both cases but only some managed to identify when the phenol group was involved correctly. A number of responses suggested that a phenoxide ion was formed with sodium carbonate but not with sodium hydroxide. The third reaction was substitution with bromine. This reaction appeared more familiar to all candidates with the majority scoring this mark. A small proportion of candidates substituted the phenol OH group or carboxylic acid group.
			Total	**3**	
5	a	i	**Number of peaks** **2 marks** 2-nitrophenol **AND** 3-nitrophenol have **six** peaks/environments/types of carbon ✓ 4-nitrophenol has **four** peaks/environments/types of carbon ✓ **Statement** **1 mark** 4-nitrophenol can be distinguished **OR** 2-nitrophenol and 3-nitrophenol cannot be distinguished ✓	**3**	**IGNORE** any numbers shown on structures **ALLOW** 1 mark only **IF** a response identifies that all the compounds have 6 peaks/environments/types of C **OR** all the compounds have 4 peaks/environments/types of carbon **IGNORE** chemical shifts **DO NOT ALLOW ECF** from an incorrect number of peaks/environments/types of carbon **<u>Examiner's Comments</u>**

					This question required candidates to apply their knowledge of ^{13}C NMR spectroscopy to deduce the number of different carbon environments in each of the nitrophenols shown. The best responses were succinct, stating that it is possible to distinguish 4-ntirophenol from the other two after deducing the correct number of carbon environments for each compound. Lower ability candidates' responses did not identify the symmetry in 4-nitrophenol and suggested all three compounds would produce six peaks, therefore making it impossible to distinguish between them.
		ii	(In phenol) a (lone) pair of electrons on O is(partially) delocalised/donated into the π-system / ring ✓ Electron density increases/is higher (than benzene) ✓ **ORA** (phenol) is more susceptible to electrophilic attack **OR** (phenol) attracts/accepts electrophile/HNO_3 more **OR** (phenol) polarises electrophile/HNO_3 more ✓ **ORA**	**3**	**ALLOW** the electron pair in the p-orbitals of the O atom becomes part of the π-system / ring **ALLOW** diagram to show movement of lone pair into ring **ALLOW** lone pair of electrons on O is (partially) drawn/attracted/pulled/ into π-system / ring **IGNORE** activating **IGNORE** charge density **IGNORE** electronegativity **IGNORE** phenol reacts more readily *(no reference to electrophile)* **ALLOW** NO_2^+ for electrophile **Examiner's Comments** The relative reactivity of phenol is well known by candidates at this level and the majority scored two or three marks. Candidates who did not score full marks gave imprecise or vague explanations. This included reference to 'higher charge density' or 'higher electronegativity' of the phenol ring, rather than 'higher electron density'.
	b		Curly arrow from π-bond to S in SO_3 **AND**	**3**	**ANNOTATE WITH TICKS AND CROSSES** **NOTE:** curly arrows can be straight, snake-like, etc. but **NOT** double headed or half headed arrows **1st curly arrow** must

			curly arrow from the S=O bond to O atom ✓  Correct intermediate ✓ Curly arrow from C-H bond to reform π-ring ✓  		• go to the S of SO_3 **AND** • start from, **OR** close to **circle of benzene ring**  **2nd curly arrow** must start from, **OR** be traced back to, **any part of** S=O bond and go to O  **ALLOW 2nd** curly arrow from S=O to any O in SO_3 Intermediate must have correct SO_3^- structure fully displayed **DO NOT ALLOW** the following intermediate:  π-ring must cover more than half of the benzene ring structure **AND** the correct orientation, i.e. gap towards C with SO_3^- **ALLOW** + sign anywhere inside the 'hexagon' of the intermediate. **DO NOT ALLOW** mark for intermediate if CH3 is missing **curly arrow** must start from, **OR** be traced back to, **any part of** C-H bond and go inside the 'hexagon'

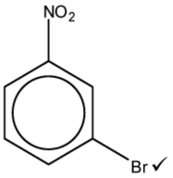
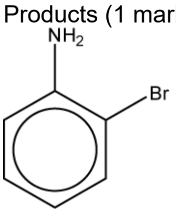
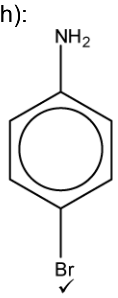
					 **<u>Examiner's Comments</u>** This question required candidates to apply their understanding of electrophilic substitution to the reaction of methylbenzene with sulfur trioxide. Examiners were encouraged by the quality of responses to this question. Most candidates secured full marks in this part. Some candidates did not show the curly arrow for the breaking of the S=O bond, while others omitted the methyl group from the intermediate. Exemplar 4 shows an excellent response. **Exemplar 4**  This response demonstrates an excellent example for candidates to follow. Curly arrows are drawn accurately, with each arrow touching the bond it starts from. The intermediate has been drawn clearly, using all the space provided. The 'horseshoe' has been drawn accurately over five of the carbon atoms with the positive charge shown neatly in the centre.
			Total	**9**	
6	a	i	**Generation of electrophile** $HNO_3 + H_2SO_4 \longrightarrow H_2O + HSO_4^- + NO_2^+$ ✓ **Electrophilic substitution**	**5**	**ANNOTATE ANSWER WITH TICKS AND CROSSES** **ALLOW** $HNO_3 + 2H_2SO_4$? $H_3O^+ + 2HSO_4^- + NO_2^+$

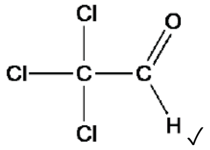
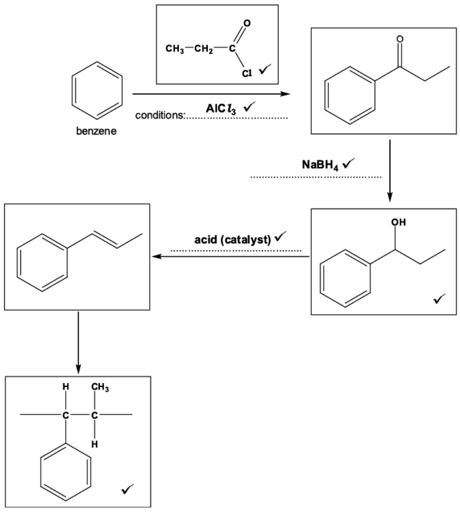
			Curly arrow from p-bond to NO_2^+ ?  --- Correct intermediate ? Curly arrow back from C-H bond to reform p-ring **AND** H^+ as product ?  **Regeneration of catalyst** $H^+ + HSO_4^- \longrightarrow H_2SO_4$ ✓		**ALLOW** $HNO_3 + H_2SO_4$?$H_2NO_3^+ + HSO_4^-$ Then $H_2NO_3^+$? $H_2O + NO_2^+$ **ALLOW** $^+NO_2$ **OR** NO_2^+ First curly arrow must come from the ring to NO_2^+ **DO NOT ALLOW** the following intermediate:  p-ring should cover approximately 4 of the 6 sides of the benzene ring structure **AND** the correct orientation, *i.e.* gap towards C with NO_2 **ALLOW** + sign anywhere inside the 'hexagon' of intermediate **Examiner Comments** The majority of candidates were well prepared for this standard mechanism and frequently scored marks of four or five. Most were able to show equations to generate the electrophile and regenerate the catalyst. Candidates should note the importance of the correct placement of curly arrows and the horseshoe in the intermediate to show the remaining electrons present in the ring structure. These were often poorly represented, leading to marks not being awarded.
		ii	*Please refer to the marking instructions on page 5 of this mark scheme for guidance on how to mark this question.* **Level 3 (5–6 marks)** Outlines the main steps of recrystallisation to produce a pure sample of 3-nitrobenzoic acid from the impure solid. **AND** Calculates correct percentage yield of 3-nitrobenzoic acid. **AND** Method of checking purity to include comparison to relevant data. *A well-structured response with the steps for recrystallisation and the determination of purity being given in the correct order. Correct use of terminology throughout.*	**6**	**Indicative scientific points, with bulleted elements, may include:** **1. Purification** • Recrystallisation • Dissolve impure solid in minimum volume of hot water/solvent • Cool solution and filter solid • Wash with cold water/solvent and dry **2. Percentage yield** • n(benzoic acid) used = $\frac{4.97}{122}$ = 0.0407 (mol)

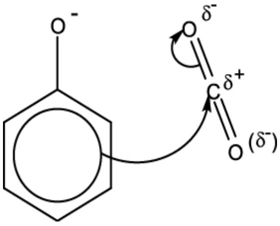
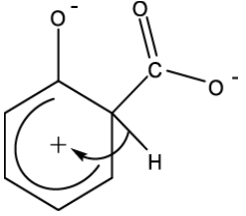
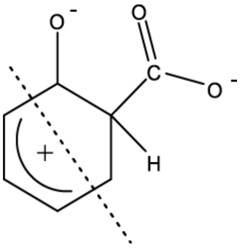
			Level 2 (3–4 marks) Attempts all three scientific points but explanations may be incomplete. **OR** Explains two scientific points thoroughly with very few omissions. *The description of checking for purity or recrystallisation is clear and any calculations structured. Key terminology used appropriately.* **Level 1 (1–2 marks)** A simple explanation based on at least two of the main scientific points. **OR** Explains one scientific point thoroughly with few omissions. *There is an attempt at a logical structure. The description of the practical techniques provides some detail but may not be in the correct order.* • *Purification step is unclear with few scientific terms and little detail, e.g. just 'recrystallise'.* • *Calculation is difficult to follow, may just include a calculation of moles of reactants and/or products.* • *Purity check specifies a method but this is unclear with little detail, e.g. take melting point.* **0 marks** No response or no response worthy of credit.		• *n*(3-nitrobenzoic acid) made = $\frac{4.85}{167}$ = 0.0290 (mol) • percentage yield = $\frac{0.0290}{0.0407} \times 100$ = 71.3 (%) **ALLOW** 71 to calculator value of 71.29001554 correctly rounded. **CHECK** for extent of errors by **ECF** Alternative correct calculation may calculate theoretical mass of 3-nitrobenzoic acid that can be produced as 0.0407 × 167 = 6.80 (g) followed by: percentage yield = $\frac{4.85}{6.80} \times 100$ = 71.3 (%) Calculation **must** attempt to calculate *n*(benzoic acid) in mol. **3. Checking purity** • Obtain melting point • Compare to known values • Pure sample will have a (sharp) melting point very close to data book value **ALLOW** alternative approach based on spectroscopy or TLC **Spectroscopy** • Run an NMR/IR spectrum • Compare to (spectral) database • Spectrum of pure sample will contain same peaks and not others **TLC** • Run a TLC • Compare (R_f value) to known data • Pure sample will have a very similar R_f **Examiner Comments** This question tested some of the practical techniques covered as part of the practical endorsement as well as requiring candidates to calculate a percentage yield for the reaction. This proved to be quite a

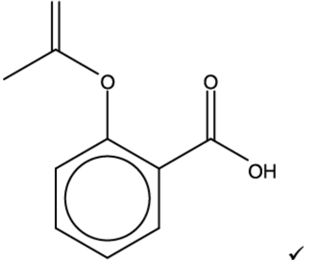
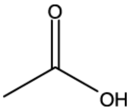
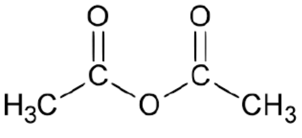
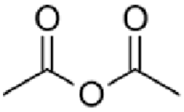
					challenging question with some candidates giving little detail of how to carry out a recrystallisation. Common answers included a statement that the solid should be allowed to dissolve in a solvent and then filtered to obtain crystals. This did not gain credit for the scientific content as there was no indication of the solid dissolving in a hot solvent and then being allowed to cool before carrying out filtration. High quality answers often went above and beyond the requirements of the marking scheme with some candidates discussing the importance of dissolving in the minimum amount of hot solvent to obtain a saturated solution, the need to wash and dry the crystals and provided detail of the apparatus and or method required. Most candidates discussed that purity could be determined by taking the melting point of the product and comparing this to a value obtained from data book. The most comprehensive answers gave an indicated of the apparatus required to carry out the melting point determination and discussed how the melting point becomes higher and sharper as impurities are removed. Common errors included comments about carrying out a boiling point determination. When carrying out a percentage yield calculation, it is important to round answers only at the last stage of the calculation. Early rounding frequently led candidates to obtain answers, which did not gain credit. Weaker Candidates divided the mass of 3-nitrobenzoic acid by the mass of benzoic acid and obtained an answer of 97.6%. Answer = 71.3%
	b	i	Phenol is the most easily nitrated/most reactive **AND** Benzoic acid is the least easily nitrated/least reactive ✓	**1**	Response **must** give rank order of reactivity e.g. nitration becomes more difficult from phenol (to benzene) to benzoic acid **OR** nitration becomes easier from right to left in the table **Examiner Comments** The vast majority of candidates gave a good answer to indicate that it was easier to carry out the nitration of phenol than

					benzene and that benzene would undergo nitration easier than benzoic acid.
		ii	**Reactivity of phenol** a (lone) pair of electrons on O is (partially) **delocalised/donated** into the p-system/ring **Reactivity of benzoic acid** The –COOH group on benzoic acid is an electron withdrawing group ✓ **Links electron density in p-bond to reactivity** In phenol electron density is higher **AND** The ring is more susceptible to attack **OR** In benzoic acid electron density is lower **AND** The ring is less susceptible to attack ✓	**3**	**ANNOTATE ANSWER WITH TICKS AND CROSSES** **ALLOW** the electron pair in the p orbitals of the O atom becomes part of the p-system / ring **ALLOW** diagram to show movement of lone pair into ring **ALLOW** lone pair of electrons on O is (partially) drawn/attracted/pulled into p-system / ring **IGNORE** activating and deactivating. **ALLOW** the following alternatives for susceptibility to attack: • phenol attracts electrophiles / NO_2^+ **more** • phenol polarises electrophiles / NO_2^+ **more** • benzoic acid attracts electrophiles / NO_2^+ **less** • benzoic acid polarises electrophiles / NO_2^+ **less** **Examiner Comments** The most able candidates scored well on what proved a difficult question for many. Although the vast majority of candidates knew about the reasons behind phenol's increased reactivity many were unable to express themselves clearly to gain credit. Often answers lacked the specific detail about the lone pair on the oxygen atom in the -OH group being delocalised into the ring. Weaker answers discussed electrons being supplied to the ring, the -OH group providing the electrons to the ring or just that -OH is an activator. Good answers expressed the increase in electron density and the subsequent increase in phenol's susceptibility to electrophilic attack. The most able candidates were able to interpret the information given in the question to establish that the -COOH group must be electron withdrawing leading to decreased electron density of the ring structure and reduced ability to react with electrophiles.

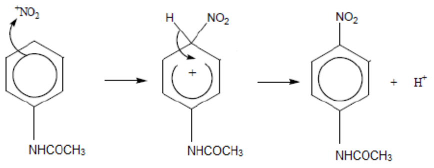
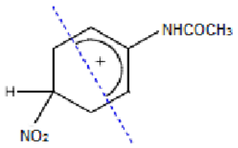
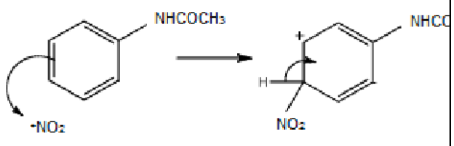
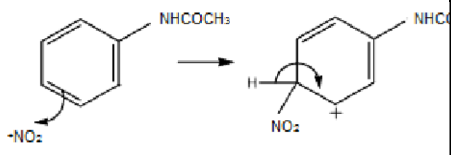
	c	i	**Bromination:** Br_2 **AND** $AlBr_3$/$FeBr_3$/Fe ✓ **Intermediate**  **Reduction:** Sn **AND** (concentrated) HCl ✓	**3**	**ALLOW** any combination of skeletal **OR** structural **OR** displayed formula as long as unambiguous **ALLOW** any suitable halogen carrier catalyst **ALLOW** Kekulé structure **IGNORE** names *(question asks for formulae)* **IGNORE** reaction conditions even if incorrect **IGNORE** 'dilute' for HCl **IGNORE** H_2 **IGNORE** NaOH if seen as a reagent to convert nitro group into amine e.g 'Sn/(concentrated) HCl then NaOH' scores the mark **Examiner Comments** Candidates were able, in the main, to provide the reagents for bromination and reduction. The structure of the intermediate compound in the preparation of 3-bromophenylamine proved to be straightforward, however common errors involved the omission of the halogen carrier catalyst for bromination or stating names rather than formulae as indicated in the question.
		ii	NH_2 is 2,4 directing ✓ Products (1 mark for each):  ✓  ✓	**3**	**IGNORE** references to electron donating/withdrawing groups **ALLOW** $–NH_2$ activates the ring causing the new group to join at positions 2 and 4. **ALLOW** ortho and para directing for 2,4 directing **IGNORE** 6-directing **ALLOW** Kekulé structure **IGNORE** names **Examiner Comments** The most able candidates completed this question with a clear statement that the $–NH_2$ group was 2,4 directing and provided two clearly drawn structures of 2-bromophenylamine and 4-bromophenylamine. The most common errors observed included drawing two structures that were identical and explaining the two structures in terms of electron donation from the $–NH_2$

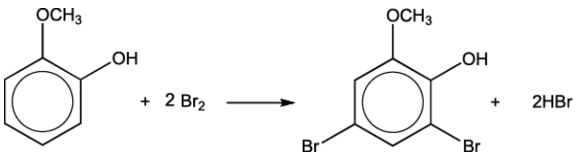
					without any indication of positioning. Candidates using the terms ortho and para directing were awarded full marks for their answers.
			Total	**21**	
7		i		1	**ALLOW** any combination of skeletal **OR** structural **OR** displayed formula as long as unambiguous
		ii	Any **organic** reaction in which sulfuric acid is a catalyst e.g: Elimination of (H_2O from) alcohols Nitration of benzene Esterification Hydrolysis of esters/amides	1	The answer needs to refer to the reaction: i.e. 'Elimination', 'hydrolysis' are insufficient but 'Esterification' describes the reaction **DO NOT ALLOW** oxidation for alcohols/ aldehydes
			Total	**2**	
8	a		One mark for each correct structure/reagent/condition as shown below 	6	**ANNOTATE ANSWER WITH TICKS AND CROSSES** **ALLOW** any combination of skeletal **OR** structural **OR** displayed formula as long as unambiguous **IGNORE** names of organic compounds *(question asks for structures)* **ALLOW** aluminium(III) chloride **OR** aluminium trichloride **ALLOW** $FeCl_3$ **OR** Fe as halogen carrier in first step. **ALLOW** sodium borohydride **OR** sodium tetrahydridoborate **IGNORE** [H] for reducing agent in second step **ALLOW** H^+ / H_2SO_4 / H_3PO_4 / named mineral acid for reagent in third step
	b		Use as an organic feedstock ✓	1	**ALLOW** the production of plastics or monomers

			OR Combustion for energy production ✓		or new polymers Combustion alone is **not** sufficient
			Total	**7**	
9	a	i	Dipole shown on C=O bond, $C^{\delta+}$ and $O^{\delta-}$, **AND** curly arrow from the C=O bond to the $O^{\delta-}$ atom **AND** Curly arrow from π−bond to C in CO_2 ✓  Correct intermediate ✓ Curly arrow back from C–H bond to reform π−ring ✓ 	3	**ANNOTATE ANSWER WITH TICKS AND CROSSES** **DO NOT ALLOW** the following intermediate:  π−ring must cover more than 1/2 of the ring **AND** 'horseshoe' in the correct orientation, *ie* gap towards C with COO^- **ALLOW** + sign anywhere inside the 'hexagon' of intermediate
		ii	Neutralisation ✓ (In Stage 1) phenol loses H^+ **AND** (In Stage 3) carboxylate ion gains H^+ ✓	2	**ALLOW** acid-base **ALLOW** both Stage 1 **AND** Stage 3 involve proton transfer
		iii	**FIRST CHECK THE ANSWER ON THE ANSWER LINE** **IF** answer = 7.31 (g) award 3 marks	3	**ANNOTATE ANSWER WITH TICKS AND CROSSES** **ALLOW ECF** at each stage

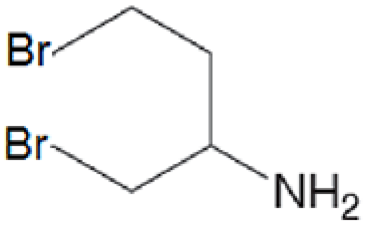
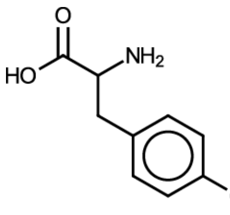
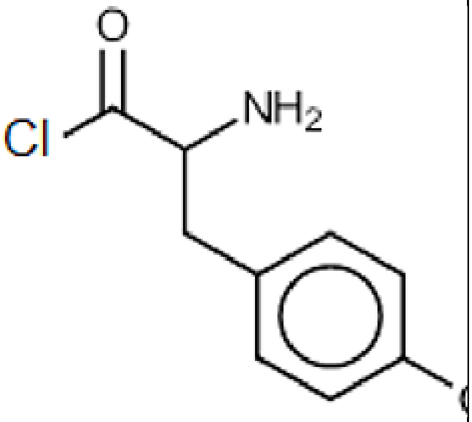
			actual n(salicylic acid) produced = $\frac{4.83}{138}$ = 0.035(0) (mol) ✓ **theoretical** n(phenol) = n(salicylic acid) = 0.035(0) × $\frac{100}{45.0}$ = 0.0778 (mol) ✓ Mass of phenol = 0.0778 × 94.0 = 7.31 (g) ✓		**ALLOW 3 SF** up to calculator value correctly rounded for intermediate values 100 **ALLOW** expected mass compound **E** = 4.83 × $\frac{100}{45.0}$ = 10.733 (g) **ALLOW** Mass phenol reacted = 0.035 × 94.0 = 3.29 (g) **ALLOW** Mass of phenol used = 3.29 × $\frac{100}{45.0}$ = 7.31 (g) **Note:** 1.48 g would get 2 marks *(use of 45.0/100 instead of 100/45.0)* 7.30 g would get 2 marks *(use of 0.0777 for moles phenol)*
	b		Skeletal formula of aspirin  ✓ Skeletal formula of ethanoic acid  ✓	2	**IF** skeletal formulae are not used **ALLOW** one mark if both the structures of aspirin **AND** ethanoic acid are correct **IGNORE** names
			Total	**10**	
1 0		i	<u>Ethanoic anhydride</u>  ✓ <u>Other organic compound</u> CH_3COOH ✓	2	**ALLOW** skeletal formula  **ALLOW** correct structural **OR** displayed

					OR skeletal formulae **OR** a combination of above as long as unambiguous **IGNORE** names **Examiner's Comments** The structure of ethanoic anhydride was well known and most candidates gave the correct structure for the other organic product of the reaction.
		ii	**FIRST CHECK THE ANSWER ON THE ANSWER LINE** **IF** answer = 2.66 (g) award 3 marks **IF** answer = 4.36 (g) award 2 marks (% yield not used) **IF** answer = 7.14 (g) award 2 marks (% yield used incorrectly) n(phenylamine) (= 3.00/93.0) = 0.0323 mol ✓ n(compound A) = (0.0323 x 0.61) = 0.0197 mol ✓ Mr (compound A) = 135 **AND** Mass of compound A = (135)(0.0197) = 2.66 g ✓ **OR** n(phenylamine) (= 3.00/93.0) = 0.0323 mol ✓ Mr (compound A) = 135 **AND** Theoretical mass of compound A = (0.0323 × 135) = 4.36 ✓ Actual mass of compound A = (4.36 × 0.61) = 2.66 g ✓	3	**ANNOTATE WITH TICKS AND CROSSES ETC.** **ALLOW 3 SF:** 0.0323 up to calculator value of 0.032258064 correctly rounded **ALLOW 3 SF** up to calculator value Penalise rounding to 2 SF once **ALLOW ECF** on incorrectly rounded values Final answer must be expressed to 3 significant figures **ALLOW** ecf from incorrect Mr **IF** answer = 2.65 (g) award 2 marks unless this alternative method is used (3 marks) 93 g gives 135 g 3.00 g gives 135/93 x 3.00 = 4.35 g 4.35 x 0.61 = **2.65** g **Examiner's Comments** Once again it was clear that candidates had been well prepared for this type of percentage yield question. It was well answered with almost all candidates scoring some marks here and a high proportion gaining all three marks for the calculation.

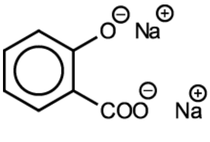
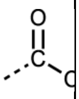
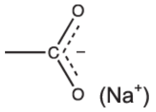
		iii	**M1** $H_2SO_4 + HNO_3$ $\rightarrow HSO_4^- + H_2O + NO_2^+$ ✓ **M2** curly arrow from πring **OR** from within the ring to $^+NO_2$ ✓  **M3** correct intermediate (with charge) ✓ **M4** curly arrow from C-H to reform ring **AND** correct products✓ **M5** Regeneration of the catalyst: $H^+ + HSO_4^- \longrightarrow H_2SO_4$ ✓	5	**ANNOTATE WITH TICKS AND CROSSES ETC.** Equation to show formation of the electrophile **ALLOW** $2H_2SO_4 + HNO_3 \longrightarrow 2HSO_4^- + H_3O^+ + NO_2^+$ **ALLOW** $H_2SO_4 + HNO_3 \longrightarrow HSO_4^- + H_2NO_3^+$ **AND** $H_2NO_3^+ \longrightarrow H_2O + NO_2^+$ Penalise missing or incorrect -NHCOCH$_3$ on intermediate only (**M3**) **DO NOT ALLOW** intermediate with the π-system covering less than half the ring  **ALLOW** + charge anywhere inside the ‘horseshoe’ Horseshoe must have open end towards NO$_2$ **ALLOW** Kekulé mechanism  **OR**  **ALLOW** $H_3O^+ + HSO_4^-$ $\longrightarrow H_2SO_4 + H_2O$

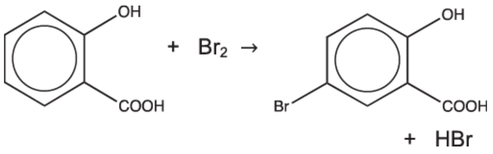
					Examiner's Comments Although some lost marks through minor errors on the details, most candidates scored well on this question
			Total	**10**	
11			 ✓	1	**ALLOW** correct structural **OR** displayed **OR** skeletal formulae **OR** a combination of above as long as unambiguous **ALLOW** disubstitution at any positions on benzene ring **Examiner's Comments** Generally well answered. Some candidates reacted compound B with only one mole of bromine or three moles of bromine and this underlines the importance of paying careful attention to information given in the stem of the question. Hydrogen, not HBr, was occasionally formed as the other product.
			Total	**1**	
12	a	i	**M1** p-orbitals overlap (to form pi / π-bonds) ✓ **M2** π-bond(s) are delocalised in **structure B** ✓ **M3** π-bonds are localised / between two carbons in **structure A** ✓ **M4**  **AND**  **Diagrams** show correct **position** of delocalised and localised π-bonds / π-electrons	4	**ANNOTATE ANSWER WITH TICKS AND CROSSES ETC** **IGNORE** p-orbitals overlap to form sigma bonds **ALLOW** electrons are delocalised in structure B **IGNORE B** has delocalised structure or ring (must be electrons or π-bonds) **ALLOW π**-electrons / p-orbital overlap localised / between two carbons in structure A **ALLOW** p-orbitals overlap with one other carbon **IGNORE** electrons are localised **OR structure A** has localised structure (must be π-bonds / π-electrons / p-orbital overlap) **ALLOW** labelled diagram showing overlap of p-orbitals between two carbon atoms **DO NOT ALLOW** C=C in this diagram Diagram for structure A must show the full ring for **M4 IGNORE** C=C in **M4** diagram

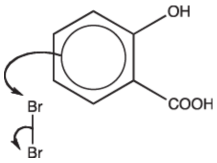
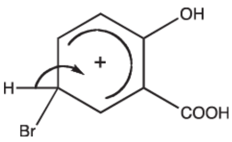
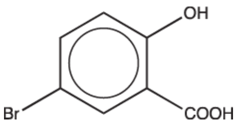
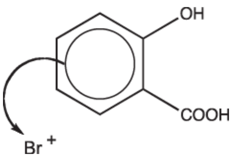
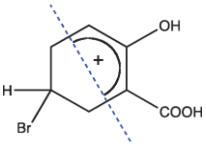
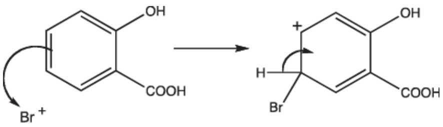
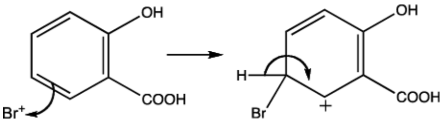
			OR correct position of p-orbital overlap ✓ ✎**QWC** requires delocalised / delocalized **spelled correctly** and used in correct context		**IGNORE** charge density **DO NOT ALLOW** electronegativity Structures do not need to be labelled A and B if the description matches the structure **Examiner's Comments** Many excellent answers with clear diagrams and explanations were seen. Delocalised electrons in structure **B** and p-orbital overlap were the most accessible marking points.
		ii	**structure B** / delocalised structure is (more) stable ✓ **structure B** is a better because (enthalpy change of hydrogenation for benzene is) less (exothermic) than (−) 357 (kJ mol^{-1}) ✓	2	**ALLOW** structure **B** is low in energy **IGNORE** structure **B** is less reactive **ALLOW** enthalpy change / hydrogenation for benzene is less (negative) than 3 × (−)119 **IGNORE** more positive than (−)357 kJ mol^{-1} **ALLOW** enthalpy change is less than 3x enthalpy change for cyclohexene **ALLOW** structure **B** is more stable by 149 kJ mol^{-1} (2 marks) **DO NOT ALLOW** more / less energy needed for the reaction Answer must refer to data given in the question and must be a comparison **IGNORE** 360 kJ mol^{-1} No marks can be awarded if structure **A** is selected **Examiner's Comments** Many used the data given in the question to compare the enthalpy of hydrogenation of structure **A** and structure **B** but relatively few candidates scored the other mark for stating that structure **B** is better representation of benzene because it is more stable. Some candidates confused cyclohexene with structure **A** and incorrectly concluded that the hydrogenation of benzene is more exothermic than structure **A**. Some incorrectly referred to enthalpy of hydration or stated that energy is required for the reaction. Others referred to data they had memorised rather than using the information in the question as instructed.

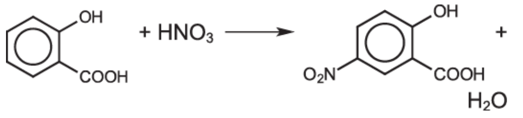
	b		$(CH_3)_2CHBr + FeBr_3 \longrightarrow (CH_3)_2CH^+ + FeBr_4^-$	1	**ALLOW** correct structural **OR** displayed **OR** skeletal formulae **OR** a combination of above as long as unambiguous **ALLOW** positive charge anywhere on the electrophile **IGNORE** $AlCl_3$ **OR** $AlBr_3$ **Examiner's Comments** Well answered by those candidates who could apply their knowledge and understanding to new situations. It was a step too far for some who stuck to the more familiar equation for the generation of the Br^+ electrophile instead. Others made a good attempt but made errors with the charges.
	c	i	First reactant = HNO_2 ✓ Second reactant =  ✓ Third reactant =  ✓	3	**ALLOW** $NaNO_2$ + HCl **OR** HNO_2 + HCl **IGNORE** conditions / concentration **ALLOW** correct structural **OR** displayed **OR** skeletal formulae **OR** a combination of above as long as unambiguous **ALLOW**  **Examiner's Comments** This question required candidates to recognise changes in chemical structure. The first reaction (the formation of a diazonium ion) and the third reaction (the formation of an amide linkage) should be

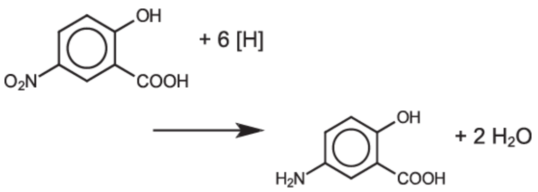
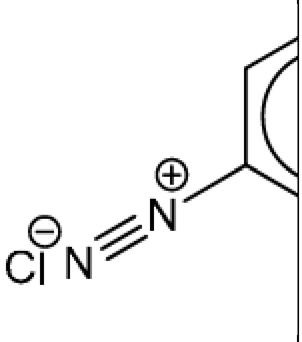
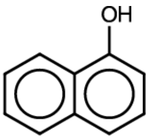
					familiar to candidates. The reagents for the first reaction were very well known and although the conditions for the reaction were often quoted they were not required for the mark. The correct structure of the second reactant was rarely seen with the most common incorrect responses being based on cyclic structures. Most candidates were able to deduce the structure of the third reactant.
		ii	**FIRST CHECK THE ANSWER ON THE ANSWER LINE** **IF** answer = 1.35 (g) award 3 marks **IF** answer = 0.54 (g) award 2 marks (no scale-up) **IF** answer = 0.216 (g) award 2 marks (incorrect scale-up) *n*(compound D) = 1.73/346 = 0.00500 mol ✓ *n*(1,3-diaminobenzene) required = 100/40 × 0.005 = 0.0125 mol ✓ Molar mass of 1,3-diaminobenzene = 108 (g mol^{-1}) **AND** Mass of 1,3-diaminobenzene = (108)(0.0125) = 1.35 g ✓	3	**ANNOTATE ANSWER WITH TICKS AND CROSSES ETC** **If there is an alternative answer, check to see if there is any ECF credit possible** **ALLOW ECF** from incorrect amount, scale-up or molar mass **Alternative 1** n(compound D) = 1.73/346 = 0.00500 mol Molar mass of 1,3-diaminobenzene = 108 (g mol^{-1}) **AND** Mass of 1,3-diaminobenzene = (0.00500)(108) = 0.540 g Mass of 1,3-diaminobenzene required = (0.540)(100/40) = 1.35 g **Alternative 2** 346 g gives 108 g 1.73 g gives 108/364 × 1.73 = 0.54 g 0.54/40 ×100 = 1.35 g **Examiner's Comments** Candidates had been well prepared for this type of percentage yield question and it was very well answered with almost all candidates scoring marks here and a high proportion gaining all three marks for the calculation.
		iii	(compound D has) **two** chiral centres ✓ Four optical isomers exist ✓ (Synthesis could) use enzymes **OR** bacteria **OR** use (chemical) chiral synthesis **OR** chiral catalysts	3	**ALLOW** (Compound **D**) has two asymmetric carbons **OR** has two stereocentres **ALLOW** four enantiomers **OR** two pairs of enantiomers **INDEPENDENT MARK** **ALLOW** biological catalysts **ALLOW** chiral transition metal complex /

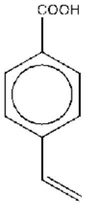
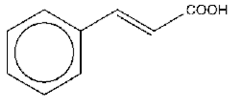
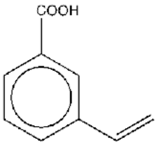
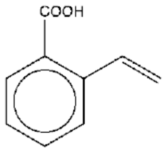
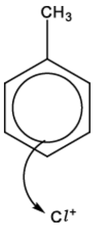
			OR use natural chiral molecules **OR** single isomers (as starting materials) ✓		catalyst **OR** stereoselective transition metal complex / catalyst **ALLOW** 'chiral pool' / chiral auxiliary **Examiner's Comments** Two chiral centres and four optical isomers was required in the mark scheme and less specific answers did not score the first two marks. Two pairs of enantiomers was an accurate description worthy of the mark and a reference to there being four enantiomers was also given credit. The majority of candidates scored only the third mark with their suggestion of how to improve the synthesis. Some candidates missed the point here and instead described techniques required to separate the optical isomers.
			Total	**16**	
13	a	i	 ✓	1	**ALLOW** correct structural **OR** displayed **OR** skeletal formulae **OR** combination of above as long as unambiguous **DO NOT ALLOW** —O—Na **OR** -COO-Na (covalent bond) **ALLOW** —O⁻ **ALLOW** —ONa **ALLOW** —COONa **OR**  **ALLOW** delocalised carboxylate  **Examiner's Comments** The question asked for the product of the reaction with excess sodium hydroxide. Many answers included the product formed by the reaction of just one of the functional groups. Most commonly the phenol group was left unreacted. The mark scheme permitted the omission of the cation from the formula of the compound but this omission was rarely seen.
		ii	(Bromine) would be decolourised / turn (from orange / red / yellow / brown) to colourless	1	**IGNORE** goes clear

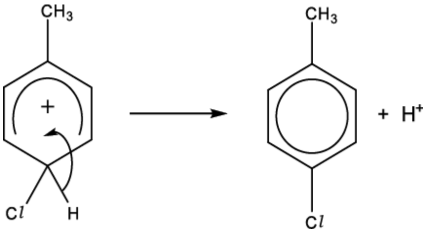
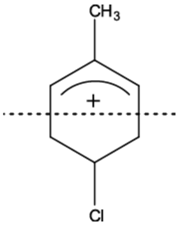
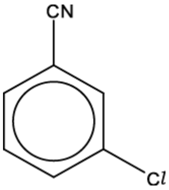
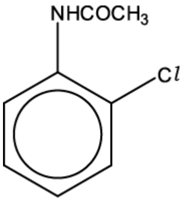
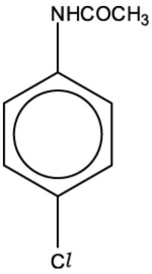
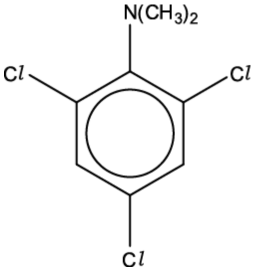
			OR white precipitate / solid / emulsion (formed) ✓		**DO NOT ALLOW** other colours for bromine **IGNORE** cream precipitate **DO NOT ALLOW** salicylic acid turns colourless / decolourised **IGNORE** temperature / fumes **Examiner's Comments** The observation for the reaction of a phenol with bromine was very well known and many candidates offered two correct observations when only one was required to score the mark.
		iii	 ✓	1	**ALLOW** correct structural **OR** displayed **OR** skeletal formulae **OR** combination of above as long as unambiguous **MUST** be all correct to score mark **ALLOW** molecular formulae, i.e. $C_7H_6O_3 + Br_2 \rightarrow C_7H_5O_3Br^{+}$ HBr **Examiner's Comments** A very well answered question. Most candidates copied the structural formulae given in the question. Some made errors when they unnecessarily converted the structures into molecular formulae. HBr was occasionally missing as a product.
		iv	$(CH_3)_2CHOH$ / $CH_3CH(OH)CH_3$ / propan(–)2(–)ol **AND** acid / H^+ / H_2SO_4 (catalyst) ✓	1	**ALLOW** correct structural **OR** displayed **OR** skeletal formulae **OR** combination of above as long as unambiguous **ALLOW** 2-propanol **DO NOT ACCEPT** incorrect name or incorrect formula of alcohol **IGNORE** reflux / concentrated (acid) **Examiner's Comments** Many candidates correctly gave the formula for propan-2-ol and included an acid catalyst. Common non-scoring answers omitted the acid or the alcohol or gave an incorrect name for the alcohol.

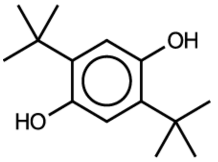
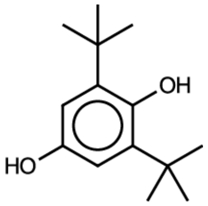
	b	i	 No Br_2 dipole needed Curly arrow to Br from ring **OR** from within the ring **AND** curly arrow Br-Br bond to Br ✓ ……………………………………………………  ✓ correct intermediate (with charge) ✓ curly arrow from C—H to reform ring  + HBr / H^++ Br^- ✓ Correct products (Br^- may be shown in the first step)	4	**ALLOW** mechanism with Br^+ electrophile (Maximum 3 marks)  **IGNORE** any equations involving a halogen carrier …………………………………………………… **BUT DO NOT ALLOW** intermediate with π-system covering less than half of ring:  **ALLOW** + charge anywhere inside the 'horseshoe' Horseshoe must have open end towards Br Apply ecf to error in structure of intermediate (M2) **ALLOW** Kekulé mechanism as shown (Maximum 3 marks if Br^+ is the electrophile)  **ALLOW** double bonds in alternate arrangement  **Examiner's Comments** Many fully correct and clearly structured mechanisms were seen. A proportion of candidates did not score full marks because they ignored the information in the question and based their mechanism on the Br^+ electrophile and did not finish

					with HBr as a product. Relatively few candidates lost marks for incorrectly positioned curly arrows.
		ii	(In salicylic acid) lone pair / pair of electrons on O(H) / phenol is ∽ (partially) **delocalised** into the ring ✓ electron density increases / is high **ORA** ✓ Br_2 / electrophile is (more) polarised **ORA** ✓ ✎**QWC**: delocalised / delocalized / delocalise *etc.* must be spelled correctly in the correct context at least once	3	**ALLOW** diagram to show movement of lone pair into ring but delocalised ring must be mentioned **ALLOW** lone pair / pair of electrons on O(H) / phenol is (partially) drawn / attracted / pulled into **delocalised** ring **IGNORE** 'activates the ring' **ALLOW** more electron rich **DO NOT ALLOW** charge density or electronegativity **ALLOW** (salicylic acid) attracts electrophiles more/more susceptible to electrophilic attack **ALLOW** Br_2 is (more) attracted OR Br_2 is not polarised by benzene **OR** induces dipoles (in bromine / electrophile) Delocalise(d) needed to score the first marking point **Examiner's Comments** This question was very well answered with the majority of candidates scoring at least two marks. The most common errors were the omitting the words delocalised or lone pair or failure to use the word delocalised in the correct context.
	c	i	**Step 1** Add HNO_3 ✓  ✓ **Step 2** Tin **AND concentrated** HC/ ✓	4	**ALLOW** reagent mark if HNO_3 in equation **IGNORE** H_2SO_4 (**NOTE**: H_2SO_4 not required with phenols) **IGNORE** concentrations of acids / temperature **ALLOW** correct structural **OR** displayed **OR** skeletal formulae **OR** combination of above as long as unambiguous Equations **MUST** be completely correct for **one** mark each

			 ✓		**DO NOT ALLOW** $3H_2$ **Examiner's Comments** This question discriminated well. Most candidates knew that nitric acid was involved in the first reaction but some also included sulfuric acid and tried to construct a mechanism involving the nitronium ion, rather than write the expected equation for the reaction. The omission of water as a product was an occasional error. Many correct equations were seen for Step 2, but tin and *concentrated* hydrochloric acid was required to score the reagent mark.
		ii	Nitrogen electron pair **OR** nitrogen lone pair accepts a proton / H^+ ✓	1	**DO NOT ALLOW** nitrogen / N lone pair accepts hydrogen (proton/H^+ required) **ALLOW** nitrogen donates an electron pair / lone pair to H^+ **IGNORE** NH_2 group donates electron pair **Examiner's Comments** Candidates needed to mention the electron pair on the nitrogen atom to score this mark.
		iii	**compound A**  ✓ compound **B**  ✓	2	**ALLOW** correct structural **OR** displayed **OR** skeletal formulae **OR** combination of above as long as unambiguous **ALLOW** $—N_2Cl$ **OR** $—N_2^+Cl^-$ **DO NOT ALLOW** $—N\equiv N^+$ **OR** $—N\equiv N^+\ Cl^-$ **DO NOT ALLOW** $—N_2$-Cl (covalent bond) **Examiner's Comments** The vast majority of candidates gave the correct structure for compound B, but common errors were the omission of the chloride ion in the formulae of the diazonium salt, or placing the positive charge on the wrong nitrogen atom.
			Total	**18**	
14			π bonds in benzene are delocalised	1	

			Total	**1**	
15			Electrophilic substitution means benzene ring Electrophilic addition means alkene / C=C Isomer of $C_9H_8O_2$ containing C=C, benzene ring **AND** COOH Correct isomer:  **OR**  justification in terms of number of carbon environments	5	Concluded using data provided and conclusions from 1st two marks. **ALLOW** 1 mark for:  **OR**  (does not gain final justification mark)
			Total	**5**	
16	a		**Experimental evidence – ANY TWO from** carbon–carbon bond lengths are the same in benzene Enthalpy change of hydrogenation is less (exothermic) for benzene (than for Kekulé model) Discussion of named reaction to highlight greater stability, e.g. chlorination of benzene requires a catalyst whereas no catalyst is needed for alkenes **Bonding in modern model** p-orbitals overlap to form π bonds (π−)electrons are delocalised	4	**ALLOW** both marks for correctly labelled diagrams showing overlap of p-orbitals to form delocalised π–electrons
	b		**Generation of electrophile** $AlCl_3 + Cl_2 \rightarrow AlCl_4^- + Cl^+$ **Electrophilic substitution** Curly arrow from π-bond to Cl^+  Correct intermediate	5	**ANNOTATE ANSWER WITH TICKS AND CROSSES** **DO NOT ALLOW** the following intermediate:

			Curly arrow back from C-H bond to reform π-ring **AND** H^+ as product  **Regeneration of catalyst** $H^+ + AlCl_4^- \rightarrow AlCl_3 + HCl$		 π-ring must be more than 1/2 way down **AND** ‘horseshoe’ the right way, *i.e.* gap towards C with Cl **ALLOW** + sign anywhere inside the ‘hexagon’ of intermediate
	c	i	 	3	**IGNORE** names throughout **DO NOT ALLOW** poly-substituted products **DO NOT ALLOW** 2-chloro or 4-chloro products **DO NOT ALLOW** 3-chloro product
		ii		1	
		iii	(In $C_6H_5N(CH_3)_2$) (lone) pair of electrons on N is (partially) **delocalised** into the ring electron density increases / is higher (than in benzene) **ORA** Cl_2 / electrophile is (more) polarised **ORA**	3	**ALLOW** diagram to show movement of lone pair into ring but **delocalised** ring must be mentioned **ALLOW** lone pair of electrons on N is (partially) drawn / attracted / pulled into **delocalised** ring **DO NOT ALLOW** charge density or electronegativity **ALLOW** Cl_2 is (more) attracted **OR** Cl_2 is not polarised by benzene

					OR induces dipoles (in chlorine / electrophile)
			Total	**16**	
17		i	 **OR** 	1	**ALLOW** correct structural **OR** displayed **OR** skeletal formulae **OR** a combination of above as long as unambiguous **ALLOW** disubstituted compound with *tert*-butyl groups adjacent
		ii	(The student's friend is correct because) the lone pair of electrons on the oxygen atom(s) is donated to / partially delocalised into the π system making quinol more susceptible to electrophilic attack	3	**ALLOW** "the oxygen p-orbital overlaps with…" **ALLOW** diagrammatic answer for 1st and 2nd marks: 1st mark: π system **OR** 6 × p orbitals shown 2nd mark: O lone pair **OR** O p-orbital **AND** interaction **ALLOW** undergoes electrophilic substitution more easily if 1st and 2nd marks achieved through diagram, conclusion **must** refer to diagram for 3rd mark
			Total	**4**	