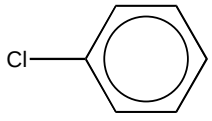
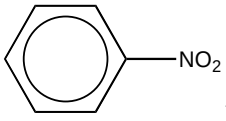
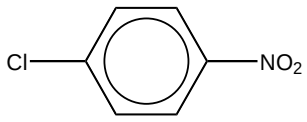
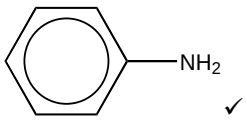
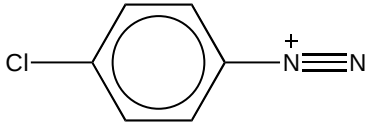
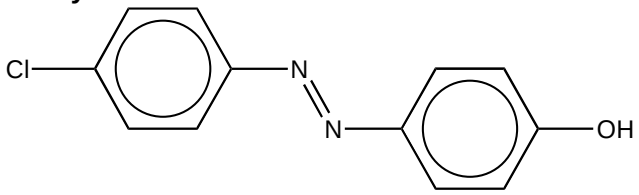
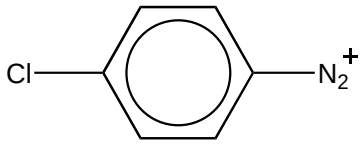
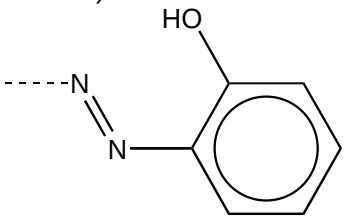
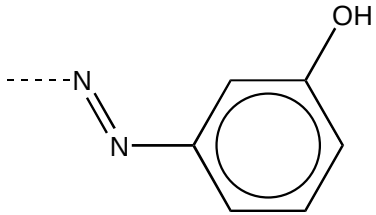
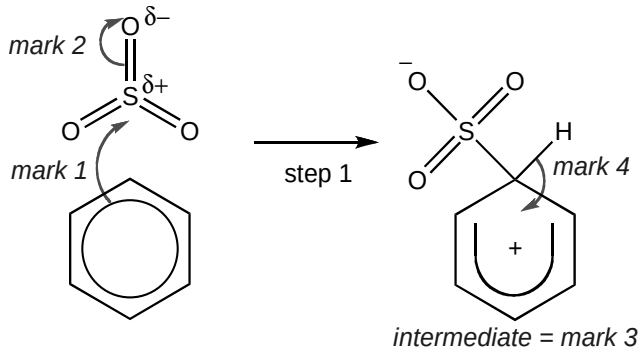
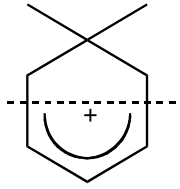
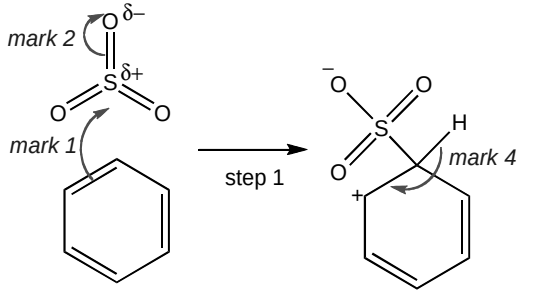
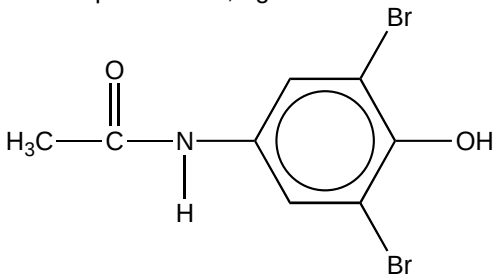
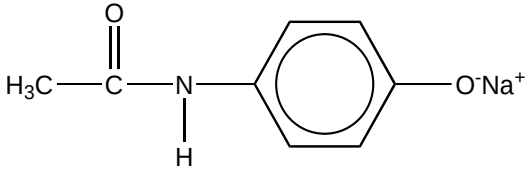
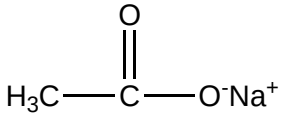
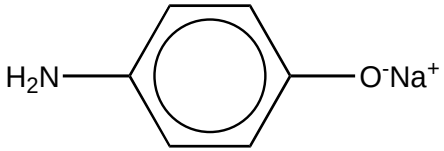
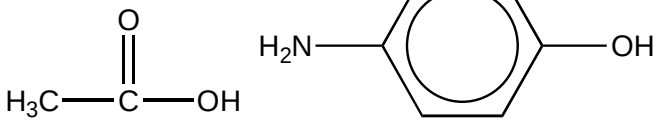
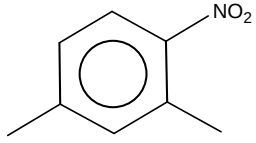
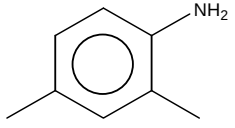
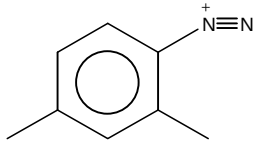
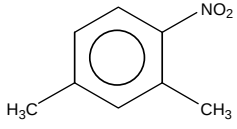
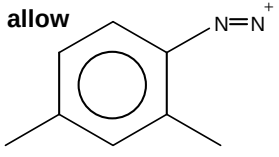
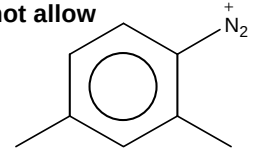
Question			er	Mark	Guidance
1	(a)	(i)	Response requires three stages • chlorination • nitration • reduction Reduction must be **a later stage** than nitration **Mark according to which sequence chosen.** **Stage 1** **organic product:**  **OR**  ✓ **chemicals:** Cl_2 **AND** $AlCl_3$ **OR** HNO_3 **AND** H_2SO_4 ✓ **Stage 2** **organic product:**  **OR**  ✓ **chemicals:** HNO_3 **AND** H_2SO_4 **OR** Sn **AND** HCl ✓ **Stage 3** **chemicals:** Cl_2 **AND** $AlCl_3$ **OR** Sn **AND** HCl ✓	5	Acceptable sequence of stages are: • nitration, reduction, chlorination • nitration, chlorination, reduction, • chlorination, nitration, reduction For organic products, **ALLOW** $C_6H_5NO_2$ **OR** C_6H_5Cl **OR** $C_6H_5NH_2$ **ALLOW** NO_2– **AND** NH_2– **DO NOT ALLOW** $ClC_6H_4NO_2$ (formula ambiguous) **DO NOT ALLOW** molecular formulae **IGNORE** any **additional** structures shown eg 2- (*ortho*) and 3- (*meta*) substituted isomers In chemicals boxes, **IGNORE** temperatures **IGNORE '**catalyst' For **chlorination** chemicals, **ALLOW** Cl_2 **AND** $FeCl_3$ **OR** Cl_2 **AND** Fe **OR** Cl_2 **AND** halogen carrier For **nitration** chemicals, 'concentrated' **not** required for HNO_3 OR H_2SO_4 **BUT** ... **DO NOT ALLOW** 'dilute' For **reduction** chemicals, 'concentrated' HCl **not** required but **DO NOT ALLOW** 'dilute' For Sn/HCl **ALLOW** addition of NaOH also **IF** it is clear that it is a second step **BUT** ……. **DO NOT ALLOW** Sn **AND** HCl **AND** NaOH **IGNORE** catalyst

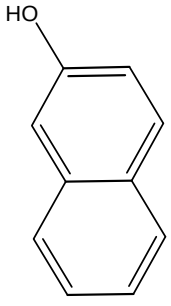
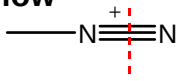
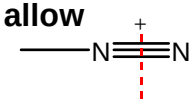
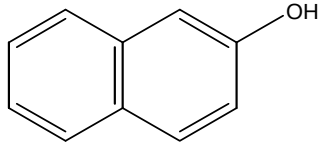
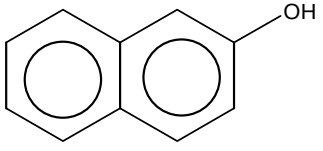
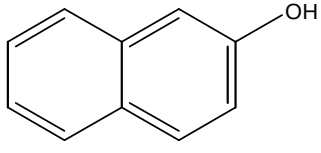
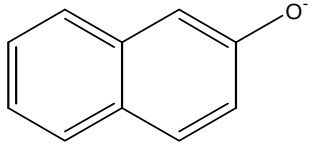
Question			er	Mark	Guidance
	(a)	(i	**diazonium ion**  ✓ –N≡N group **MUST** be displayed **azo dye**  ✓ –N=N– group **MUST** be displayed	2	**ALLOW** '+' sign up to halfway along triple bond from left-hand N **IGNORE** presence of Cl^- **DO NOT ALLOW** $Cl^{-}-$ substituent on benzene ring **DO NOT ALLOW:**  **In azo dye,** **ALLOW** as alternative to phenol OH group: O^- **OR** O^-Na^+ **OR** ONa **ALLOW** phenol part substituted at any carbon (ie 2,3 or 4 position for –OH) i.e.   **IGNORE** geometry/shape, i.e. **ALLOW** —N=N— **Mark independently** **DO NOT ALLOW** if Cl– is missing from benzene ring in **EITHER** structure

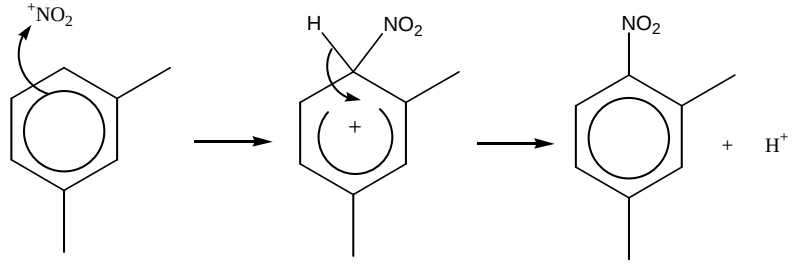
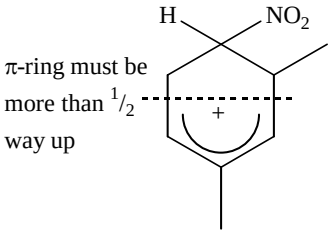
Question			er	Mark	Guidance
	(b)			4	***ANNOTATIONS MUST BE USED*** **mark 1** – curly arrow from π-delocalised ring in benzene to $S^{\delta+}$ in SO_3 ✓ **ALLOW** curly arrow from the ring **OR** from within the ring **mark 2** – curly arrow from **one** S=O double bond to the O (to produce a $S–O^-$) ✓ **ALLOW** curly arrow to any O in SO_3 **mark 3** – intermediate showing delocalisation over 5 carbons ✓ Intermediate must have correct SO_3^- structure **FULLY** displayed **DO NOT ALLOW** intermediate with broken ring less than halfway up in correct orientation:  **mark 4** – curly arrow from C–H bond reforming π- delocalised ring in benzene ✓ **Stand alone mark** **IGNORE** responses after **STEP 2**

Question			er	Mark	Guidance
					ALLOW Kekulé mechanism  **ALLOW** double bonds shown in other Kekulé arrangement
	(c)	(i)	Various possibilities, eg:  ✓	2	**ALLOW** 1, 2, 3 or 4 Br atoms substituted on phenol ring at carbon atoms 2, 3, 5 or 6 **BUT** –OH must be in correct position shown **DO NOT ALLOW** O^- or ONa **ALLOW** for side chain: CH_3CONH but aromatic part of structure must be shown **IGNORE** any additional inorganic products in boxes (even if incorrect
			Reaction with Na  ✓		**ALLOW** ONa **OR** O^- as alternative to O^-Na^+ **DO NOT ALLOW** O–Na **OR** O^-Na (i.e. Na without charge) –ONa must be in correct position shown **ALLOW** for side chain: CH_3CONH but aromatic part of structure must be shown **IGNORE** any additional inorganic products in boxes (even if incorrect)

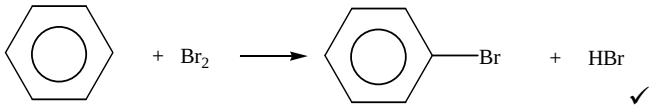
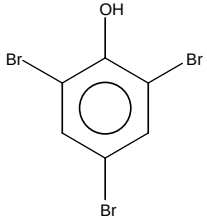
Question			er	Mark	Guidance
	(c)	(ii)	**Hydrolysis with NaOH(aq)**  ✓  ✓ **Mark independently**	2	On **BOTH** structures, **ALLOW** ONa **OR** O^- as alternative to O^-Na^+ **DO NOT ALLOW** O–Na **OR** O^-Na (i.e. Na without charge) –ONa must be in correct position shown on 2nd structure **ALLOW** CH_3COONa/ CH_3CO_2Na **OR** CH_3COO^-/ $CH_3CO_2^-$ **ALLOW** one mark for carboxylic acid **AND** phenol, rather than sodium salts:  **ALLOW** NH_2–, CH_3– **IGNORE** any additional inorganic products in boxes (even if incorrect)
			Total	**15**	

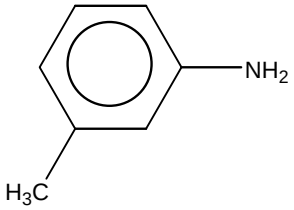
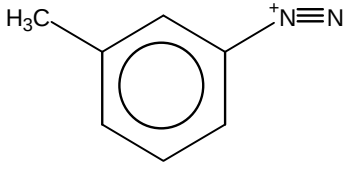
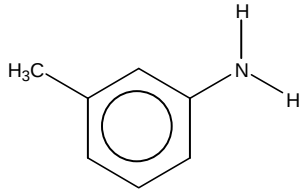
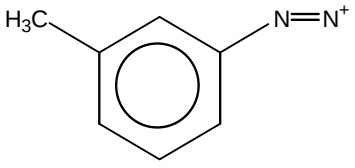
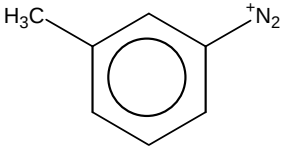
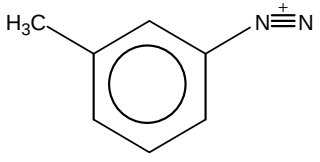
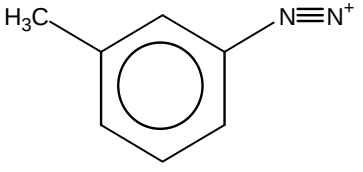
Question			Expected Answers	Marks	Additional Guidance
2	a		Bond length intermediate between/different from (short) C=C and (long) C–C ✓ ΔH hydrogenation less exothermic than expected (when compared to ΔH hydrogenation for cyclohexene) ✓ Only reacts with Br_2 at high temp or in presence of a halogen carrier / resistant to electrophilic attack ✓ **Please annotate, use ticks to show where marks are awarded**	3	**ALLOW** all carbon–carbon bonds the same length **ALLOW** ΔH hydrogenation less (negative) than expected **ALLOW** ΔH hydrogenation different from that expected **DO NOT ALLOW** ΔH halogenation/hydration **ALLOW** doesn't decolourise/react with/polarise Br_2 **ALLOW** doesn't undergo addition reactions (with Br_2)
	b	i	compound **A**  if NO_2 in wrong position penalise here and ECF for rest of **b(i)** and **b(ii)** ✓ compound **B**  ✓ compound **C**  ✓	4	**ALLOW** any 4-nitro-1,3-dimethylbenzene drawn in any orientation **ALLOW**  drawn in any orientation **ALLOW** any 4-amino-1,3-dimethylbenzene drawn in any orientation **ECF** amine of incorrect compound **A** (e.g. position of NO_2 or lack of methyl sticks/groups) **ALLOW** diazonium chloride salt of 1,3-dimethylbenzene **ECF** diazonium salt/compound of incorrect compound **B** **IGNORE** Cl^- ion **allow**  **not allow** 

Question	Expected Answers	Marks	Additional Guidance
	compound **D**  ✓		**ALLOW** if + charge is floating between the two Ns only if it is closer to the correct N **allow**  **not allow**  **ALLOW** any of     **ALLOW** O^- in place of OH

Question	Expected Answers	Marks	Additional Guidance
ii	***mark 1*** $HNO_3 + 2H_2SO_4 \rightarrow H_3O^+ + 2HSO_4^- + NO_2^+$ ✓ ***mark 4*** – curly arrow from C–H bond back to reform π ring **AND** correct products ✓  ***mark 2*** – curly arrow from π ring to $^+NO_2$ ✓ ***mark 3*** – intermediate with π ring broken in the correct place ✓ ***mark 5*** - $H^+ + HSO_4^- \rightarrow H_2SO_4$ ✓ Link to compound **A** in part **(i)** – cannot score full marks [in **b(i)** & **b(ii)**] if NO_2 is not adjacent to a methyl	5	Equation to show formation of NO_2^+ ion ✓ **ALLOW** $HNO_3 + H_2SO_4 \rightarrow H_2O + HSO_4^- + NO_2^+$ $HNO_3 + H_2SO_4 \rightarrow HSO_4^- + H_2NO_3^+ \rightarrow H_2O + NO_2^+$ **ALLOW** mark 2 curly arrow must be from 1,3-dimethylbenzene to NO_2^+ and **ECF** for marks 3 and 4 **DO NOT ALLOW** intermediate  **ALLOW** CH_3s shown **ALLOW** $H_3O^+ + HSO_4^- \rightarrow H_2O + H_2SO_4$
iii	2 ✓	1	No other correct response
	Total	**13**	

If NO_2 is in correct position do not penalise even if compound **A** in **b(i)** is not in correct position

Question			Expected Answers	Marks	Additional Guidance
3	(a)		 ✓	1	**ALLOW** $C_6H_6 + Br_2 \longrightarrow C_6H_5Br + HBr$ **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 and bubbles **DO NOT ALLOW** $Br_3C_6H_2OH$ **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** $C_6H_{10}Br_2$ **OR** structures
		(iii)	**MUST** spell delocalised/delocalized or localised/localized correctly once in the answer to obtain all 5 marks **benzene** electrons or π-bonds are delocalised ✓ **phenol** a lone or non-bonded 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** $Br^{\delta+}$ **OR** electrophile Br^+ as alternate to polarise

	(c)		 ✓  ✓✓ **ALLOW** ECF ✓✓ on incorrect amine HNO_2 + HCl and temp < 10 ^oC **OR** $NaNO_2$ + HCl and temp < 10 ^oC ✓ alkaline **AND** phenol (if temperature stated must be below 10 ^oC) ✓	**5**	**ALLOW**  **IGNORE** Cl^- ion **DO NOT ALLOW** if ring is connected to the N triple bond in the diazonium or if diazonium has a negative charge **ALLOW** one mark for correct displayed diazonium if alkyl group is not shown **ALLOW**  for both marks **ALLOW**  for one mark **ALLOW**  for one mark **ALLOW**  for one mark **ALLOW** NaOH **OR** KOH & C_6H_5OH **OR** phenoxide ion **OR** $C_6H_5O^-$ **ALLOW** reagents and conditions from the equations
			Total	**14**	