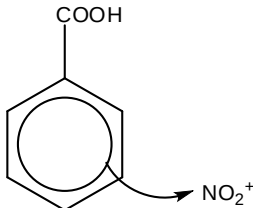
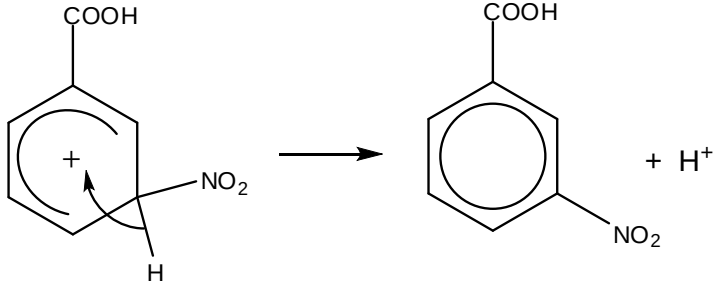
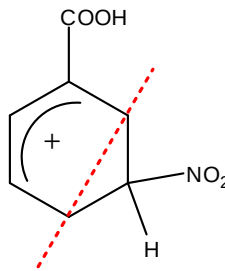
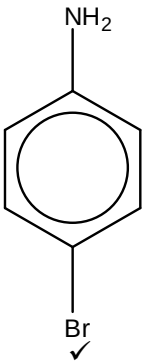
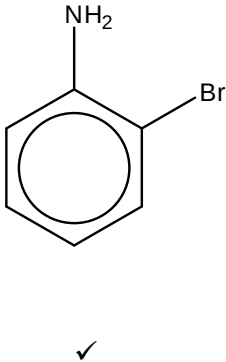


Question	Answer	Marks	Guidance
1 (a) (i)	Generation of electrophile $\text{HNO}_3 + \text{H}_2\text{SO}_4 \longrightarrow \text{H}_2\text{O} + \text{HSO}_4^- + \text{NO}_2^+ \checkmark$ Electrophilic substitution Curly arrow from π-bond to NO_2^+ $\checkmark$  ----- Correct intermediate $\checkmark$ Curly arrow back from C-H bond to reform π-ring AND H^+ as product $\checkmark$  Regeneration of catalyst $\text{H}^+ + \text{HSO}_4^- \longrightarrow \text{H}_2\text{SO}_4 \checkmark$	5	ANNOTATE ANSWER WITH TICKS AND CROSSES ALLOW $\text{HNO}_3 + 2\text{H}_2\text{SO}_4 \rightarrow \text{H}_3\text{O}^+ + 2\text{HSO}_4^- + \text{NO}_2^+$ ALLOW $\text{HNO}_3 + \text{H}_2\text{SO}_4 \rightarrow \text{H}_2\text{NO}_3^+ + \text{HSO}_4^-$ then $\text{H}_2\text{NO}_3^+ \rightarrow \text{H}_2\text{O} + \text{NO}_2^+$ ALLOW $^+\text{NO}_2$ OR NO_2^+ First curly arrow must come from the ring to NO_2^+ DO NOT ALLOW the following intermediate:  π-ring should cover approximately 4 of the 6 sides of the benzene ring structure AND the correct orientation, <i>i.e.</i> gap towards C with NO_2 ALLOW + sign anywhere inside the 'hexagon' of intermediate

2	(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
	(ii)	Reactivity of phenol a (lone) pair of electrons on O is (partially) delocalised/donated into the π -system / ring ✓	3	ANNOTATE ANSWER WITH TICKS AND CROSSES 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

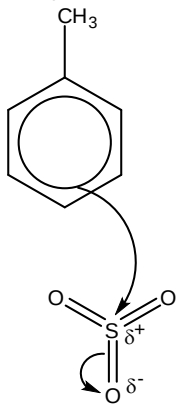
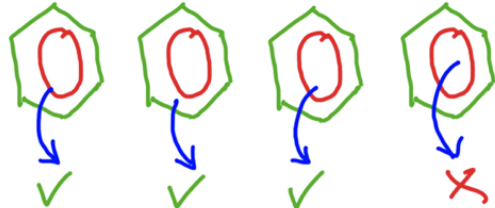
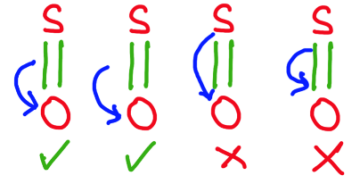
Question	Answer	Marks	Guidance
	Reactivity of benzoic acid The –COOH group on benzoic acid is an electron withdrawing group ✓ Links electron density in π-bond to reactivity In phenol electron density is higher AND The ring is more susceptible to attack OR In benzoic acid electron density is lower AND The ring is less susceptible to attack ✓		ALLOW lone pair of electrons on O is (partially) drawn/attracted/pulled into π-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

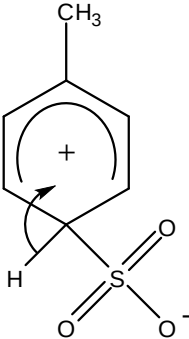
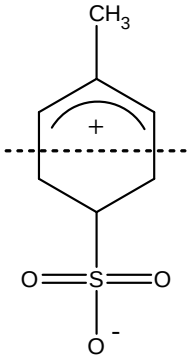
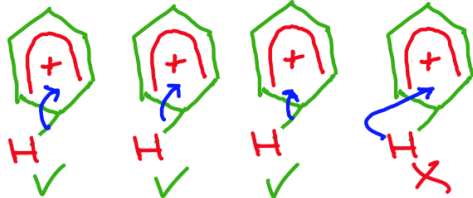
	3	NH₂ is 2,4 directing ✓ Products (1 mark for each): 	3	IGNORE references to electron donating/withdrawing groups ALLOW –NH₂ activates the ring causing the new group to join at positions 2 and 4. ALLOW ortho and para directing for 2,4 directing IGNORE 6-directing ALLOW Kekulé structure IGNORE names
		Total	21	

Question	Answer	Marks	Guidance
4	C	1	

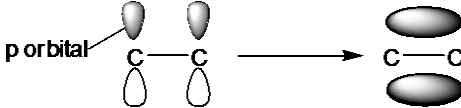
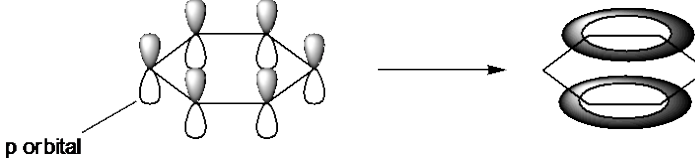
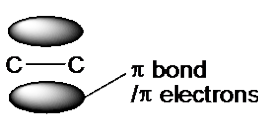
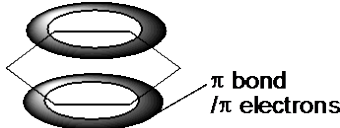
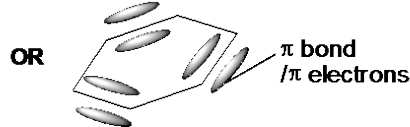
Question	Answer	Marks	Guidance
5	A	1	

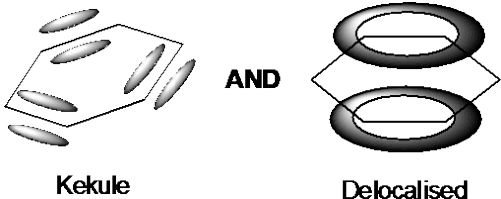
	6	(In phenol) a (lone) pair of electrons on O is (partially) delocalised/donated into the π-system / ring ✓ Electron density increases/is higher (than benzene) ✓ ORA (phenol) is more susceptible to electrophilic attack OR (phenol) attracts/accepts electrophile/HNO_3 more OR (phenol) polarises electrophile/HNO_3 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 (<i>no reference to electrophile</i>) ALLOW NO_2^+ for electrophile
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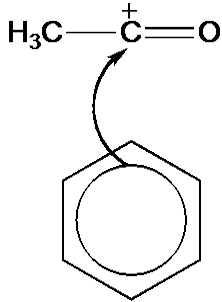
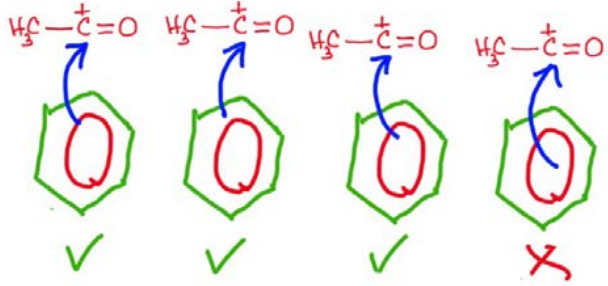
Question	Answer	Marks	Guidance
7	Curly arrow from π-bond to S in SO_3 AND curly arrow from the S=O bond to O atom ✓ 	3	ANNOTATE WITH TICKS AND CROSSES NOTE: curly arrows can be straight, snake-like, etc. but NOT double headed or half headed arrows 1st curly arrow must - go to the S of SO_3 AND - start 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

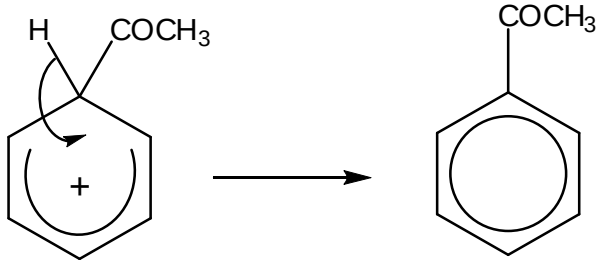
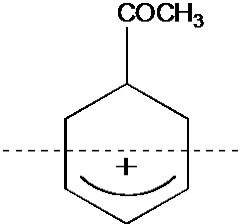
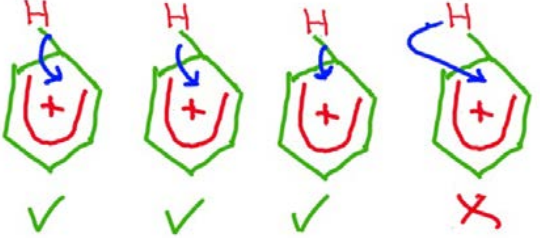
Question	Answer	Marks	Guidance
	Correct intermediate ✓ Curly arrow from C-H bond to reform π-ring ✓ 		DO NOT ALLOW the following intermediate:  π-ring must cover more than half of the benzene ring structure AND the correct orientation, <i>i.e.</i> gap towards C with SO_3^- ALLOW + sign anywhere inside the 'hexagon' of the intermediate. DO NOT ALLOW mark for intermediate if 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' 
	Total	9	

Question	Answer	Marks	AO	Guidance
8	C	1	AO1.2	

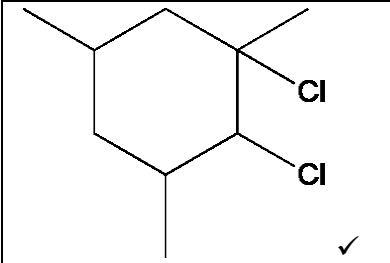
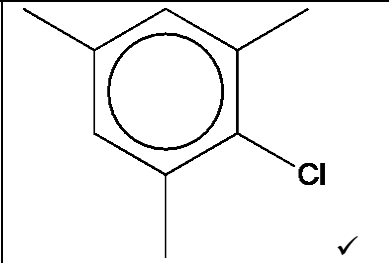
Question		Answer	Marks	element	
9	(a) (i)	Similarities Orbital overlap (sideways) overlap of p orbitals ✓ π bond π bond/system/ring above and below (bonding (C) atoms/ring/plane) ✓	3	AO1.1 × 3	ANNOTATE ANSWER WITH TICKS AND CROSSES ETC ALLOW diagram showing orbital overlap e.g. p orbital  OR  p orbital label is required for first mark IGNORE C=C in diagram showing π bond IGNORE reference to s orbital overlap/σ bonds ----- ALLOW from labelled diagram showing π bond e.g.  OR  OR  π bond/π electrons label is required for second mark

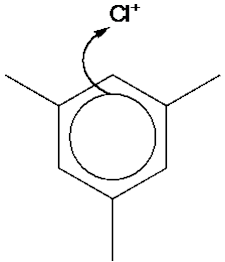
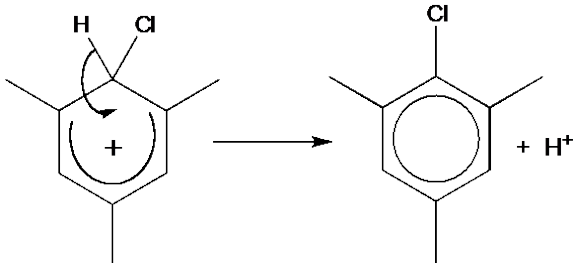
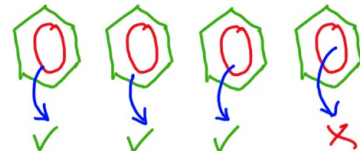
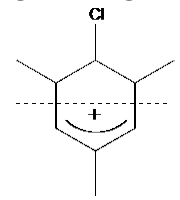
Question	Answer	Marks	element	
	Difference Kekule has: alternating π bonds OR 3 π bonds / localised (π electrons) / overlap in one direction / 2 electrons in π bond AND Delocalised has: π ring (system) / all p orbitals overlap OR (π electrons) spread around ring / overlap in both directions / 6 electrons in π bond /			----- ALLOW diagram showing π bond in both Kekule AND delocalised models e.g  Kekule AND Delocalised π bond labels not required for third mark
(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	AO1.1 ×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, AlCl₃, FeBr₃

	10	Formation of electrophile $\text{CH}_3\text{COCl} + \text{AlCl}_3 \rightarrow \text{CH}_3\text{-C}^+=\text{O} + \text{AlCl}_4^- \checkmark$ Mechanism Curly arrow from π-bond to $\text{CH}_3\text{C}^+=\text{O}$ $\checkmark$  -----	5	AO2.5 AO2.5	ANNOTATE ANSWER WITH TICKS AND CROSSES ALLOW '+' charge anywhere on $\text{CH}_3\text{C}^+\text{O}$ i.e. CH_3CO^+ NOTE: curly arrows can be straight, snake-like, etc. but NOT double headed or half headed arrows 1st curly arrow must - go to the C of $\text{C}=\text{O}$ AND - start from, OR close to circle of benzene ring  IGNORE curly arrow shown on $\text{C}=\text{O}$
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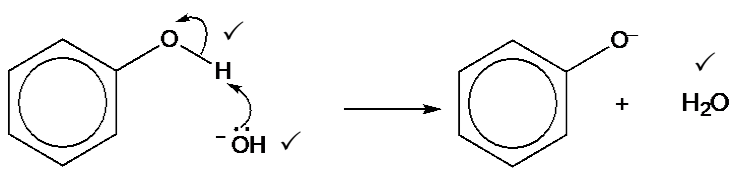
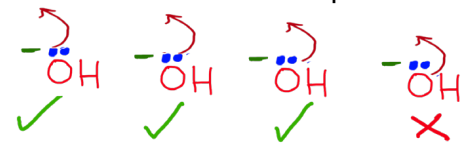
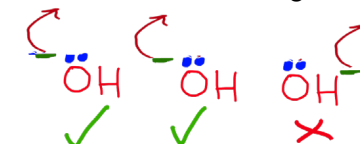
Question	Answer	Marks	element	
	Correct intermediate ✓ Curly arrow from C–H bond to reform π-ring ✓  Regeneration of catalyst $\text{H}^+ + \text{AlCl}_4^- \longrightarrow \text{AlCl}_3 + \text{HCl} \checkmark$		AO3.1 AO2.5 AO1.2	DO NOT ALLOW the following intermediate:  π-ring should cover approximately 4 of the 6 sides of the benzene ring structure AND the correct orientation, <i>i.e.</i> gap towards C with COCH_3 ALLOW + sign anywhere inside the 'hexagon' of intermediate curly arrow must start from, OR be traced back to, any part of C-H bond and go inside the 'hexagon' 

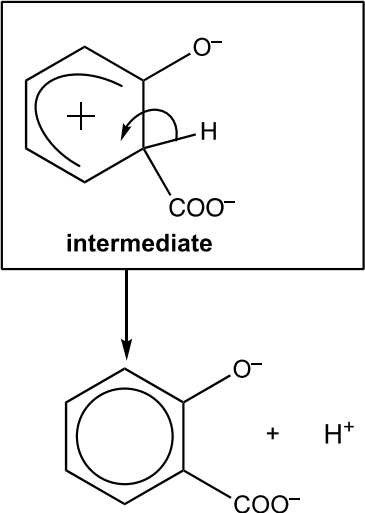
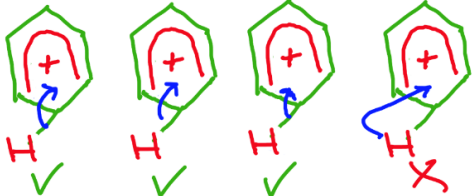
Question	Answer	Marks	AO	Guidance
11	C	1	1.2	

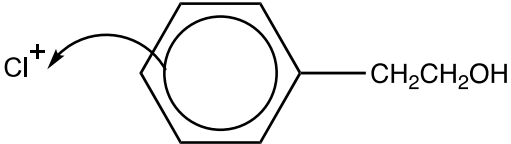
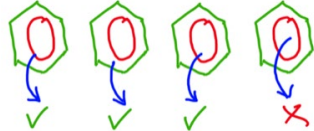
Question			Answer	Marks	element	Guidance
12	(a)	(i)	 Organic product with B  Organic product with C	2	2.5×2	
		(ii)	Reactivity of B in B electrons are localised OR in B π-bond is localised ✓ Reactivity of C in C electrons are delocalised OR In C π-system / ring is delocalised In B, electron density is 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	1.1×3	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

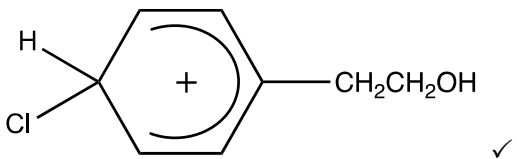
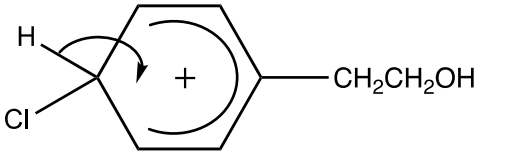
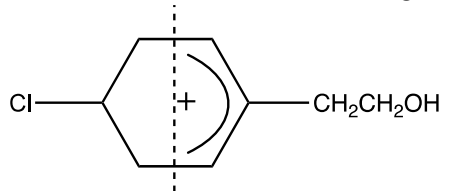
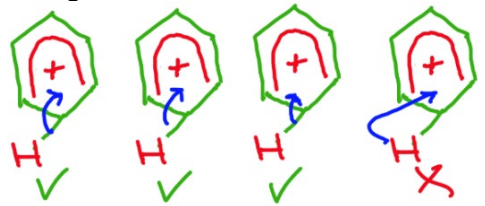
Question	Answer	Marks	element	Guidance
(iii)	Generation of electrophile $\text{AlCl}_3 + \text{Cl}_2 \rightarrow \text{AlCl}_4^- + \text{Cl}^+ \checkmark$ Attack of Cl^+  Curly arrow from π-bond to Cl^+ $\checkmark$ Intermediate and organic product  Correct intermediate $\checkmark$ Curly arrow from C–H bond to reform π-ring $\checkmark$ Regeneration of catalyst $\text{H}^+ + \text{AlCl}_4^- \rightarrow \text{AlCl}_3 + \text{HCl} \checkmark$	5	1.2 1.2 2.5 1.2 1.2	ANNOTATE ANSWER WITH TICKS AND CROSSES ALLOW $\text{FeCl}_3 + \text{Cl}_2 \rightarrow \text{FeCl}_4^- + \text{Cl}^+$ 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  DO NOT ALLOW following intermediate:  π-ring must cover 4 of the 6 sides of the benzene ring AND correct orientation, <i>i.e.</i> gap towards C–Cl ALLOW + sign anywhere inside the 'hexagon' of the intermediate.

Question	Answer	Marks	AO element	Guidance
13	C	1	AO1.1	

Question	Answer	Marks	element	Guidance
14 (a) (i)	Stage 1  1 mark for each curly arrow as shown.	6	AO1.1 AO1.2 AO2.5	ANNOTATE WITH TICKS AND CROSSES NOTE: curly arrows can be straight, snake-like, etc. but NOT double headed or half headed arrows Curly arrow from OH⁻ must - go to the H of O-H AND - start from, OR be traced back to any point across width of lone pair on O of OH⁻  OR start from – charge⁻OH ion  Curly arrow from O–H bond must start from, OR be traced back to, any part of O–H bond and go to O IGNORE dipoles on O–H bond IGNORE Na⁺

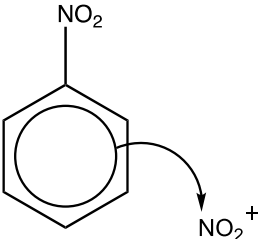
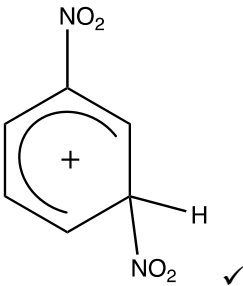
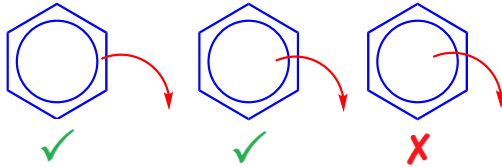
Question	Answer	Marks	element	Guidance
	 intermediate + H⁺			DO NOT ALLOW mark for intermediate if phenolic O⁻ is missing curly arrow must start from, OR be traced back to, any part of C-H bond and go inside the 'hexagon' 
(ii)	OH⁻: base ✓ CO₂: electrophile OR electron pair acceptor ✓	2	AO2.1 ×2	ALLOW alkali IGNORE 'nucleophile', 'donates electron pair' IGNORE lone pair acceptor (<i>No lone pair involved</i>)

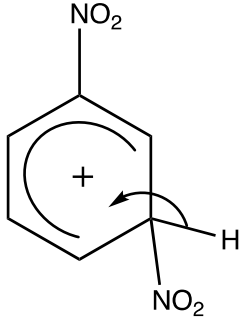
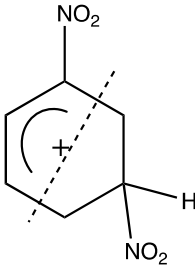
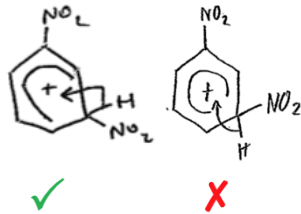
Question			Answer	Marks	AO element	Guidance
15	(a)	(i)	Indicator AND observation of acidity AND No reaction with carbonate ✓	1	AO1.2 ×1	ALLOW (Add) bromine AND white precipitate ✓ ALLOW (Add) FeCl ₃ AND violet/purple colour ✓
15	(a)	(ii)	ANNOTATE ANSWER WITH TICKS AND CROSSES Action of catalyst 1 mark Formation of electrophile: $\text{Cl}_2 + \text{AlCl}_3 \rightarrow \text{Cl}^+ + \text{AlCl}_4^-$ AND Regeneration of catalyst: $\text{H}^+ + \text{AlCl}_4^- \rightarrow \text{AlCl}_3 + \text{HCl}$ ✓ ----- Electrophilic attack 1 mark Curly arrow from π-bond to Cl^+ ✓ 	4	AO1.2 ×2 AO2.5 ×2	ALLOW use of FeCl₃ or other halogen carriers (AlBr₃) ----- For curly arrows, ALLOW straight or snake-like arrows and small gaps (see examples): ----- 1st curly arrow must - start from, OR close to circle of benzene ring AND - go to Cl^+ 

Question	Answer	Marks	element	Guidance
	Correct intermediate only 1 mark  ----- Reforming benzene ring 1 mark Curly arrow from C–H bond to reform π-ring ✓ 			DO NOT ALLOW the following intermediate:  π-ring must cover more than half of benzene ring AND correct orientation, <i>i.e.</i> gap towards C with Cl ALLOW + sign anywhere inside the 'hexagon' of intermediate DO NOT ALLOW intermediates substituted at positions 3 or 5 IGNORE intermediates substituted at position 2 OR di-substituted at positions 2,4 ----- Curly arrow must start from, OR be traced back to, any part of C–H bond and go inside the 'hexagon' 

Question			Answer	Marks	element	Guidance
15	(b)		(In phenols) a (lone) pair of electrons on O is (partially) delocalised/donated into the ring / π-system ✓ Electron density increases/is higher (than benzene) ✓ ORA (phenols) are more susceptible to electrophilic attack OR (phenols) attract/accept electrophile/Cl_2 more OR (phenols) polarise electrophile/Cl_2 more ✓ ORA	3	AO1.1 × 3	ALLOW the electron pair in the p-orbitals of the O atom becomes part of the ring / π-system ALLOW diagram to show movement of lone pair into ring ALLOW lone pair of electrons on O is (partially) drawn/attracted/pulled/ into ring / π-system ALLOW lone pair on O DO NOT ALLOW (two) lone pairs are delocalised/donated into the ring / π-system IGNORE activating IGNORE charge density IGNORE electronegativity IGNORE phenols react more readily with electrophiles/Cl_2 (<i>given in question</i>) ALLOW Cl^+ for electrophile IGNORE Cl for electrophile

Question	Answer	Marks		Guidance
16	B	1	AO1.1	

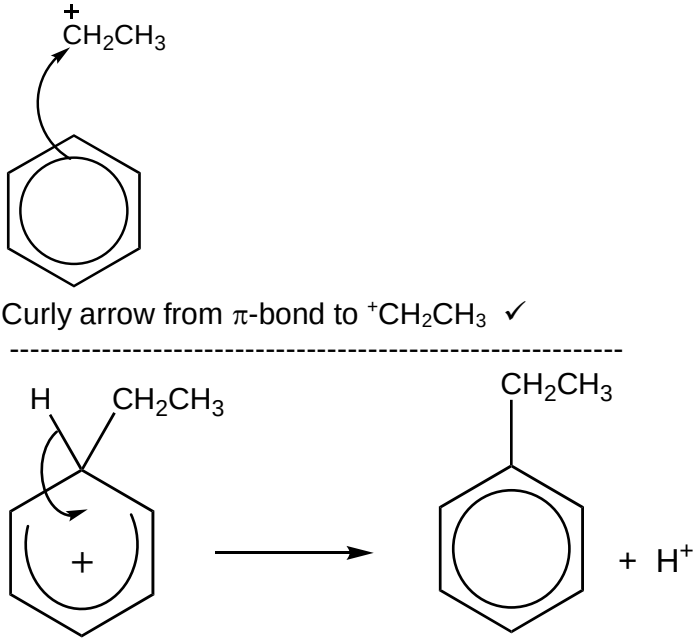
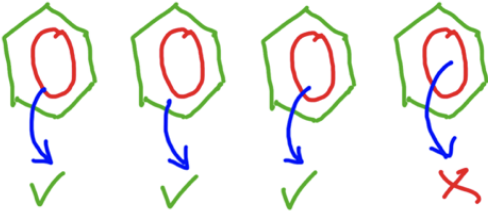
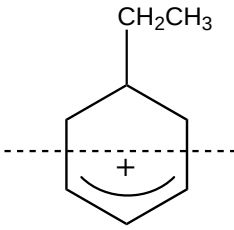
	Question	Answer	Marks	element	Guidance
17	(a)	Role of H₂SO₄ catalyst 2 marks <i>Forming electrophile</i> $\text{HNO}_3 + \text{H}_2\text{SO}_4 \longrightarrow \text{H}_2\text{O} + \text{HSO}_4^- + \text{NO}_2^+ \checkmark$ <i>Reforming catalyst</i> $\text{H}^+ + \text{HSO}_4^- \longrightarrow \text{H}_2\text{SO}_4 \checkmark$ Electrophilic attack 1 mark Curly arrow from π-bond to NO_2^+ $\checkmark$  Correct intermediate 1 mark 	5	AO1.2 AO1.2 AO1.2 AO2.5	ANNOTATE ANSWER WITH TICKS AND CROSSES ALLOW $\text{HNO}_3 + 2\text{H}_2\text{SO}_4 \rightarrow \text{H}_3\text{O}^+ + 2\text{HSO}_4^- + \text{NO}_2^+$ ALLOW $\text{HNO}_3 + \text{H}_2\text{SO}_4 \rightarrow \text{H}_2\text{NO}_3^+ + \text{HSO}_4^-$ then $\text{H}_2\text{NO}_3^+ \rightarrow \text{H}_2\text{O} + \text{NO}_2^+$ ALLOW $^+\text{NO}_2$ OR NO_2^+ 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 AND - go to anywhere on NO_2^+  DO NOT ALLOW mark for intermediate if additional NO_2 is missing

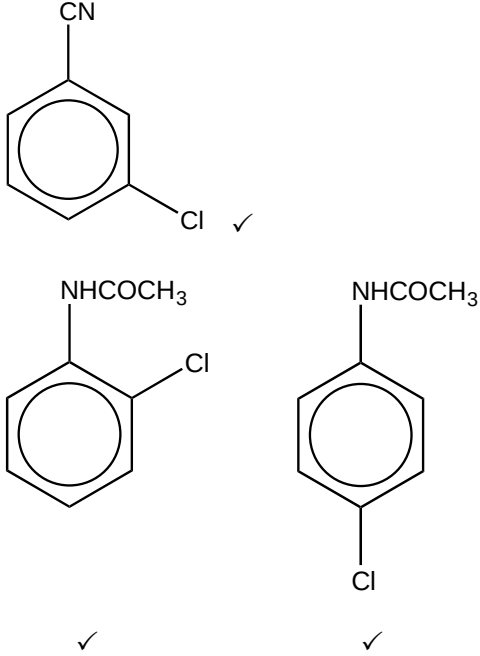
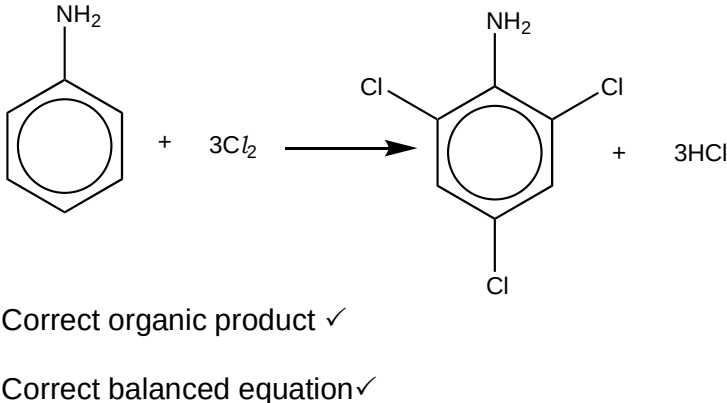
Question	Answer	Marks	element	Guidance
	----- Reforming benzene ring 1 mark Curly arrow from C–H bond to reform π-ring ✓  Curly arrow must start from, OR be traced back to, any part of C–H bond and go inside the 'hexagon'		AO1.2	IGNORE connectivity to NO₂ groups (<i>mark is for correct substitution position and position of π-ring</i>) DO NOT ALLOW the following intermediate:  π-ring should cover approximately 4 of the 6 sides of the benzene ring structure AND the correct orientation, <i>i.e.</i> gap towards C with NO₂ and H  ALLOW + sign anywhere inside the 'hexagon' of intermediate

Question		Answer	Marks	element	Guidance
17	(b)	FIRST CHECK ANSWER ON ANSWER LINE If answer = 73.2 award 3 marks Theoretical moles $n(\text{C}_6\text{H}_5\text{NO}_2)$ OR $n(\text{C}_6\text{H}_4(\text{NO}_2)_2)$ $= \frac{12.5 \times 1.20}{123.0}$ OR 0.12195... (mol) ✓ Actual moles $n(\text{C}_6\text{H}_4(\text{NO}_2)_2) = \frac{15.0}{168.0}$ OR 0.0892857(mol) ✓ % yield = $\frac{0.0892857...}{0.12195....} \times 100$ = 73.2 % to 3SF ✓	3		ALLOW 3SF up to calculator value throughout working IGNORE rounding errors past 3SF TAKE CARE as value written down may be truncated but with value stored in calculator, depending on rounding, either can be credited. AO2.8 Calculator = 0.1219512195 AO2.8 Calculator = 0.08928571429 AO1.2 ALLOW ECF except for final mark if value is $\geq 100\%$ Alternative method using mass 1. Theoretical moles = 0.12195.... mol 2. Mass = 0.12195... $\times$ 168.0 OR 20.4878... g 3. % yield = $\frac{15}{20.4878...} \times 100 = 73.2\%$ Common errors 87.9% → 2 marks From $\frac{12.5}{123} = 0.101626....$ (no density)

Question			Answer	Marks	element	Guidance
17	(c)		<u>Dissolve</u> in the <u>minimum</u> quantity of <u>hot</u> water/solvent ✓ Cool (to allow crystals form) AND Then filter (under reduced pressure) ✓ (Leave to) <u>dry</u> ✓	3	AO3.3 ×3	ALLOW any solvent IGNORE • Initial filtering • Filtration between dissolving and cooling (implies hot filtration) • Washing with cold solvent DO NOT ALLOW use of drying agent (e.g. MgSO₄)

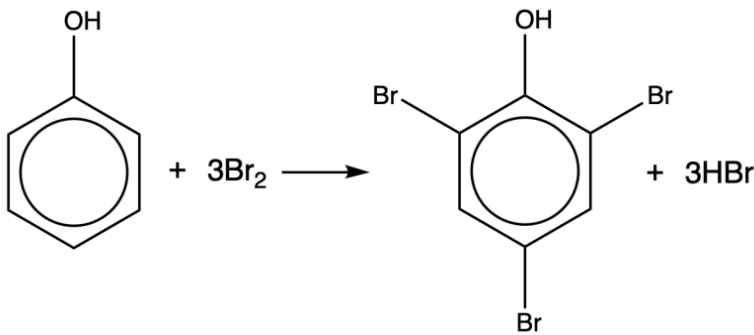
Question			Answer	Marks	Guidance
18			1-ethyl-2,4-dimethylbenzene ✓	1	ALLOW other unambiguous names using smallest numbering. e.g. ALLOW 1,3-dimethyl-4-ethylbenzene 2,4-dimethylethylbenzene ethyl-2,4-dimethylbenzene 2,4-dimethyl-1-ethylbenzene IGNORE alphabetical order of methyl and ethyl IGNORE lack of hyphens, extra hyphens, full stops instead of commas, extra spaces DO NOT ALLOW 1,5-dimethyl-2-ethylbenzene OR 1,3-dimethyl-6-ethylbenzene <i>Needs smallest numbers</i> DO NOT ALLOW the following for dimethyl: dimethy, dimeth, dimethly, dimethanyl DO NOT ALLOW the following for ethyl: ethy, eth, ethly, ethanyl

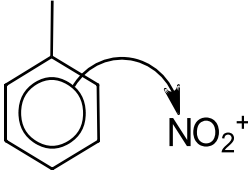
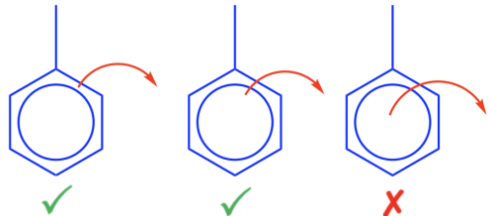
Question	Answer	Marks	Guidance
19			ALLOW correct Kekulé representation of benzene throughout question 19
19	(a) (i) An electron pair acceptor ✓	1	ALLOW gains an electron pair / lone pair
19	(a) (ii) Generation of electrophile $\text{AlCl}_3 + \text{CH}_3\text{CH}_2\text{Cl} \longrightarrow \text{CH}_3\text{CH}_2^+ + \text{AlCl}_4^-$ ✓ Electrophilic substitution  Curly arrow from π-bond to $^+\text{CH}_2\text{CH}_3$ ✓ Correct intermediate ✓ Curly arrow from C-H bond to reform π-ring AND H^+ as product ✓ Regeneration of catalyst $\text{H}^+ + \text{AlCl}_4^- \longrightarrow \text{AlCl}_3 + \text{HCl}$ ✓	5	ANNOTATE ANSWER WITH TICKS AND CROSSES ALLOW any combination of skeletal OR structural OR displayed formula as long as unambiguous ALLOW $\text{C}_2\text{H}_5\text{Cl}$ AND C_2H_5^+ ALLOW positive charge anywhere on CH_2CH_3 e.g. CH_2CH_3^+ 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 AND - go to anywhere on $^+\text{CH}_2\text{CH}_3$  DO NOT ALLOW the following intermediate:  π-ring should cover approximately 4 of the 6 sides of the benzene ring structure AND 'horseshoe' the right way, i.e. gap towards C with CH_2CH_3 ALLOW + sign anywhere inside the 'hexagon' of intermediate

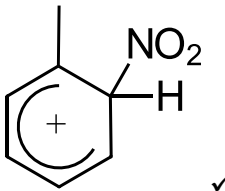
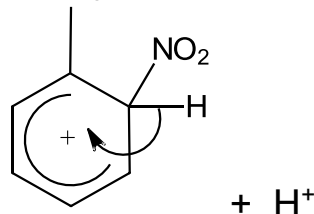
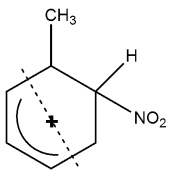
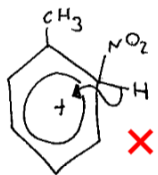
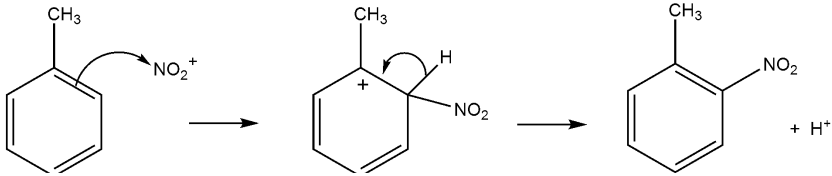
	Question	Answer	Marks	Guidance
20	(b) (i)		3	IGNORE additional copies of the same structures IGNORE connectivity to CN and NHCOCH₃ in products. IGNORE HCl / H⁺ IGNORE multisubstituted products ALLOW protonation of NHCOCH₃ group i.e. NH₂⁺COCH₃ ALLOW ECF small slips on NHCOCH₃ e.g. extra O or missing 3 on CH₃
20	(b) (ii)	 Correct organic product ✓ Correct balanced equation ✓	2	ALLOW any trichlorophenyl amine structure ALLOW C₆H₂Cl₃NH₂ OR C₆H₄Cl₃N (allow elements in any order) for correct organic product IGNORE incorrect structural or molecular formula IF correct structure is drawn ALLOW ammonium salt of trichloro product C₆H₂NH₃Cl₄ ALLOW multiples for balanced equation ALLOW 1 mark for use of Br₂ with a correctly balanced equation

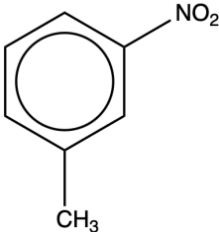
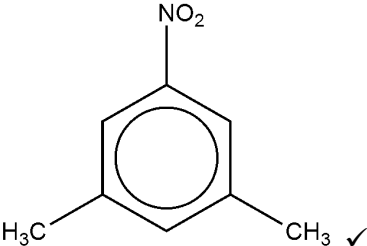
	Question	Answer	Marks	Guidance
20	(b) (iii)	(In phenylamine) a (lone) pair of electrons on N is (partially) delocalised / donated into the π-system / ring ✓ Electron density increases/is higher (than benzene) ✓ ORA (phenylamine is) more susceptible to electrophilic attack OR (phenylamine) attracts/accepts electrophile/Cl_2 more OR (phenylamine) polarises electrophile/Cl_2 more ✓ ORA	3	Must be clear that electrons come from N not just NH_2 ALLOW the electron pair (in the p-orbitals) on N atom becomes part of the π-system / ring ALLOW diagram to show movement of lone pair into ring from N ALLOW lone pair of electrons on N is (partially) drawn / attracted / pulled into π-system / ring ALLOW lone pair on N (i.e. no reference to electrons) ALLOW π-bond instead of π-system / ring DO NOT ALLOW (two) lone pairs are delocalised/donated into the π-system / ring Responses must be comparative for 2nd and 3rd marking point. IGNORE activating IGNORE charge density IGNORE electronegativity IGNORE phenylamines react more readily with electrophiles/Cl_2 (<i>given in question</i>) ALLOW Cl^+ for electrophile IGNORE Cl for electrophile ALLOW Benzene can't polarise electrophile/Cl_2 but phenylamine can (polarise electrophile/Cl_2)

Question			Answer	Mark	Guidance
21	(a)		(In the delocalised model): (C–C) bond length is between single (C–C) and double bond (C=C) OR all (C–C) bond lengths are the same ✓ (Enthalpy change of) hydrogenation is less exothermic (than expected) ✓	2	IGNORE less susceptible to electrophilic attack (given in question) DO NOT ALLOW enthalpy of hydration OR $\Delta_{\text{hyd}}H$ ALLOW 'less negative' OR 'more positive' OR 'less (heat) energy released' for 'less exothermic' IGNORE higher/lower ALLOW comparison of values that show delocalised is less exothermic e.g. Kekulé is -360 delocalised is -208
21	(b)	(i)	(In phenol) a (lone) pair of electrons on O is (partially) delocalised/donated into the ring / π-system ✓ Electron density increases/is higher (than benzene) ✓ ORA (phenol is) more susceptible to electrophilic attack OR (phenol can) attract/accept electrophile/Br_2 more OR (phenol can) polarise electrophile/Br_2 more ✓ ORA	3	ALLOW the electron pair in a p-orbital on O atom becomes part of the ring / π-system ALLOW diagram to show movement of lone pair into ring ALLOW lone pair of electrons on O is (partially) drawn/attracted/pulled/ into ring / π-system ALLOW lone pair on O DO NOT ALLOW (two) lone pairs are (partially) delocalised into ring / π-system Responses must be comparative for 2nd and 3rd marking point IGNORE activating IGNORE charge density IGNORE electronegativity ALLOW Br^+ for electrophile IGNORE Br for electrophile ALLOW Benzene can't polarise electrophile/Br_2 but phenol can (polarise electrophile/Br_2) ORA IGNORE phenol reacts more readily/easily with electrophiles

Question			Answer	Mark	Guidance
21	(b)	(ii)	 2,4,6-tribromophenol product ✓ Rest of equation and balancing ✓	2	ALLOW Kekulé structure DO NOT ALLOW substitution at any three positions on ring, must be 2, 4, 6. IGNORE molecular formula even if incorrect DO NOT ALLOW ECF for organic product with incorrect number of substituted Br (Second mark is dependent on getting first mark)
21	(c)	(i)	CH ₃ Cl AND AlCl ₃ ✓	1	ALLOW names if no formulae given ALLOW CH₃Br for reagent ALLOW AlBr₃ OR FeCl₃ OR FeBr₃ for the Lewis acid ALLOW suitable non-specification alternative Lewis acids e.g. zeolite, BF₃

Question	Answer	Mark	Guidance
21 (c) (ii)	Role of H₂SO₄ catalyst 2 marks <i>Forming electrophile</i> $\text{HNO}_3 + \text{H}_2\text{SO}_4 \rightarrow \text{NO}_2^+ + \text{HSO}_4^- + \text{H}_2\text{O} \checkmark$ <i>Reforming catalyst</i> $\text{H}^+ + \text{HSO}_4^- \rightarrow \text{H}_2\text{SO}_4 \checkmark$ Electrophilic attack 1 mark Curly arrow from π-bond to NO_2^+ $\checkmark$ 	5	ANNOTATIONS MUST BE USED ALLOW for forming an electrophile $\text{HNO}_3 + 2\text{H}_2\text{SO}_4 \rightarrow \text{NO}_2^+ + 2\text{HSO}_4^- + \text{H}_3\text{O}^+$ ALLOW for forming an electrophile $\text{HNO}_3 + \text{H}_2\text{SO}_4 \rightarrow \text{H}_2\text{NO}_3^+ + \text{HSO}_4^-$ AND then $\text{H}_2\text{NO}_3^+ \rightarrow \text{NO}_2^+ + \text{H}_2\text{O}$ NOTE: curly arrows can be straight, snake-like etc. but NOT double headed or half headed arrows ALLOW use of $^+\text{NO}_2$ OR NO_2^+ 1st curly arrow must: - start from, OR close to circle or benzene ring AND - go to anywhere on NO_2^+ 

Question	Answer	Mark	Guidance
	Correct intermediate 1 mark  Reforming benzene ring 1 mark Curly arrow from C–H bond to reform π-ring AND H^+ as product ✓ 		DO NOT ALLOW mark for intermediate if methyl group is missing, or substitution is in wrong position IGNORE connectivity (<i>mark is for correct substitution position and position of π-ring</i>) DO NOT ALLOW following intermediates:  OR  π -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 and H ALLOW + sign anywhere inside the 'hexagon' of intermediate 2nd curly arrow must: - start from, OR be traced back to any part of the C – H bond AND - go inside the 'hexagon' of the intermediate ALLOW mechanism using Kekulé structures with wheland intermediate 

Question			Answer	Mark	Guidance
21	(c)	(iii)	(Synthesis 1 shows that the) $-\text{CH}_3$ is 2, (4)-directing AND (Synthesis 2 is not successful because) $-\text{NO}_2$ / nitro group is 3-directing ✓  OR 	2	ALLOW CH_3 is 2, (4)-directing AND $-\text{NO}_2$ / nitro group is not (2, 4-directing) ALLOW $-\text{NO}_2$ / nitro group is 3-directing AND $-\text{CH}_3$ is not IGNORE CH_3 and NO_2 have different directing effects (the directing effect of at least one of the groups must be specified) ALLOW alternatives for 'directing' e.g. substitutes at ALLOW $-\text{NO}_2$ / nitro group is meta directing ALLOW $-\text{CH}_3$ is ortho, (para) directing IGNORE 5-directing for $-\text{NO}_2$ IGNORE 6-directing for $-\text{CH}_3$ ALLOW Kekulé structure